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# ACTIVATED SILICA IN WASTEWATER COAGULATION

W. J. Weber, Jr., et al

Michigan University

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# ACTIVATED SILICA IN WASTEWATER COAGULATION,

W. J. Weber, Jr. and L. H. Ketchum, Jr.

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--The role of activated silica in coagulation of wastewaters with lime was examined. Laboratory studies were conducted on synthetic wastewaters to simulate certain wastewater characteristics and verification studies were conducted on samples of natural waters and wastewaters. For high alkalinity wastewaters activated silica provides no substantial benefit; reasons for the loss of effectiveness are discussed. For low alkalinity wastewaters however, significant (3 to 10-fold) reduction in lime requirement is possible; the addition necessary to accomplish this lime reduction is small, 2 to 4 mg/l as $SiO_2$. In low alkalinity wastewaters high in phosphate concentration (approximately 7 mg/l as $PO_4$) coagulation is accomplished with low lime addition only; multinuclear, is as effective and in most cases more effective than activated silica. Activated silica-lime coagulation carries no risk of adding foreign materials to the treated water in the event of chemical carry-over; and it adds no anionic salts to the treated water, only hydroxide is added which may be neutralized by acids if the resulting pH is too high. This treatment scheme is proposed for low alkalinity wastewaters; it may provide a convenient method of treating storm and combined sewer discharges which are commonly low in alkalinity. (EM)

silica

--*Waste water treatment, *Coagulation, *Silica, Lime, *Alkalinity, Phosphates, Calcium, Sewage treatment, Storm water

--*Activated silica, *Lime treatment, Low alkalinity waste waters, *Chemical treatment

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# ABSTRACT

This investigation examined the role of activated silica in coagulation of wastewaters with lime. Laboratory studies were conducted on synthetic wastewaters made to simulate certain wastewater characteristics and verification studies were conducted on samples of natural waters and wastewaters. It was found that for high alkalinity wastewaters activated silica provides no substantial benefit in reducing the lime required for coagulation. For low alkalinity wastewaters however, significant ( 3 to 10-fold ) reduction in lime requirement is possible with activated silica. The addition necessary to accomplish this lime reduction is small, 2 to 4 mg/l as $SiO_2$. A mechanism is proposed, and reasons for the loss of effectiveness in high alkalinity wastewaters are discussed.

Two other important observations are discussed. First, in low alkalinity wastewaters high in phosphate concentration (approximately 7 mg/l as $PO_4$) coagulation is accomplished with low lime addition without need for activated silica. This is attributed to the formation of hydroxylapatite which appears to aid lime coagulation. The second observation is that multinuclear silica, a stable species found in a certain pH-concentration domain of sodium silicate solutions, is as effective and in most cases more effective than activated silica prepared by the usual methods, thus eliminating the preparation, storage, and handling problems normally associated with the use of activated silica.

Because calcium and silica are present in most natural waters at relatively high concentrations, the use of activated silica-lime coagulation carries no risk of adding foreign materials to the treated water in the event of chemical carry-over. Another important advantage to the use of lime, is that it adds no anionic salts to the treated water, only hydroxide is added which may be neutralized by acids if the resulting pH is too high.

This treatment scheme is proposed for use on low alkalinity wastewaters, which are found in the northeastern, northwestern, and some southern sectors of the United States. In addition, it may provide a convenient method of treating storm and combined sewer discharges which, due to the low alkalinity of the rain water, are commonly low in alkalinity.

This report was submitted in fulfillment of Project Number 16050 DUW under sponsorship of the Environmental Protection Agency by the Environmental and Water Resources Engineering Program, University of Michigan, Ann Arbor, Michigan 48104

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# CONCLUSIONS

The chemical combination of lime and activated silica proved to be an effective means for clarifying low alkalinity wastewaters, or more precisely, wastewaters low in total carbonate species. Under most pH conditions found in wastewaters the carbonate species would exist primarily as bicarbonate. The upper limit of bicarbonate concentration where activated silica demonstrates significant --3 to 10-fold--lime reduction is about $10^{-3}$ moles per liter (50 mg/l as $CaCO_3$). Natural waters low in alkalinity would also be low in hardness which usually accompanies alkalinity. In the synthetic systems studied, alkalinity was added in the form of sodium bicarbonate, therefore even the high alkalinity systems contained essentially no hardness. The effect of hardness may therefore be eliminated as the cause of loss of effectiveness of the lime-activated silica treatment of high alkalinity systems.

The minimum required activated silica concentration to accomplish this reduction in lime dosage is low, in the range of 2 to 4 mg/l $SiO_2$. High concentrations of activated silica, for example 14 mg/l $SiO_2$ as shown in

Figure V-1, fail to provide lime reduction. The cause for this loss of effectiveness is unclear. Possibly it is associated with colloid stability promoted by high surface coverage by activated silica. Detailed investigations of this effect were not made since activated silica additions would be made at low concentrations based on economic considerations and the range of effective application is rather broad, 2 mg/l to 12 mg/l $SiO_2$, as shown in Figure V-1.

The chapter titled "Coagulation Theory" is a summary of the current status of theories of coagulation-flocculation, based on a literature study. It was intended to be used to assist in interpreting observed experimental results, and not for the purpose of experimentally verifying theory. The synthetic and natural systems of concern in this study, for the most part, and due primarily to their heterogeneity, fall well outside the limitations imposed by these theories. The exact mechanism of clarification of these low alkalinity wastewaters using lime and activated silica was not determined. However, it is likely that calcium ions accumulate in the electrical double layer of the negatively charged colloids causing a reduction in zeta potential, or a compression of the electrical double layer. Additional calcium combines with the carbonate to form fine colloidal-size calcium carbonate precipitate. Activated silica probably then combines with the calcium carbonate precipitate and the negatively charged colloids in this state of lowered zeta potential to provide interconnection between particles until they grow sufficiently large to settle.

Apparently, when phosphates are present at levels above 7 to 10 mg/l as $PO_4$ as shown in Figure V-23, hydroxylapatite, which is relatively large and fast settling, is formed. These particles, through enmeshment or adsorption remove the negatively charged colloids and clarification is accomplished without the need for activated silica.

The reason no reduction by activated silica of the lime requirement is observed when high alkalinity waters are treated is the formation of relatively massive amounts of fine colloidal calcium carbonate precipitate. Under these conditions a high dose of calcium is required to precipitate the carbonate and yet provide free calcium ions for colloid destabilization, and nominal additions of activated silica have no significant effect on this type of system.

In those cases where effective clarification was observed when using activated silica with low concentrations of lime but not with slightly higher concentrations it is probable that the excessive amounts of free calcium tied up the active sites of the activated silica, preventing the latter from combining with the colloids. Then, at even higher lime dosages, clarification is again accomplished by the massive calcium dosage, in which case the activated silica has little effect.

Activated silica appears to be effective throughout a wide range of polymer sizes ranging from relatively small multinuclear species of only a few silicon atoms up to the very large particles formed just prior to gel formation. It appears likely that solutions can be prepared which fall in the pH-concentration domain designated as stable multinuclear shown in Figure III-2, and either used immediately or stored indefinitely. These solutions should contain sufficient concentrations of multinuclear species, which appear to perform as well as, or better than, those activated according to the usual procedures.

Chemical costs vary throughout the country. In the Midwest, for example, pebble lime (94% CaO) is available in large quantities (i.e., 80-ton hoppered-railroad cars and 22-ton trucks) at approximately $22.00 per ton. Activated silica costs approximately $0.70 per mg/l per million gallons of water treated, based on estimates by Philadelphia Quartz Company*, a major supplier of sodium silicate solutions. As shown in Figure VI-8, $2 \times 10^{-3}$ moles per liter of lime or $7.5 \times 10^{-4}$ moles per liter of lime plus 3.75 mg/l (as $SiO_2$) may be used to coagulate this low alkalinity wastewater. Based on these dosages and the above costs the chemical costs per million gallons of wastewater treated using lime alone and lime plus activated silica are $11.92 and $8.72, respectively. This chemical cost saving and the decreased sludge volume to be handled, as shown in Figure VI-10, make the use of activated silica economically advantageous.

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*Public Ledger Building, Independence Square, Philadelphia, Pennsylvania 19106

# RECOMMENDATIONS

The lime-activated silica treatment is suitable for clarification of wastewaters low in alkalinity. These types of wastewaters are known to exist in the northeastern, northwestern, and some of the southern states. Complete treatment, or treatment to a level equal to or greater than obtained with biological treatment, should be possible when the lime-activated silica treatment is followed by adsorption on carbon and possibly filtration.

Stormwaters, which are ordinarily low in alkalinity, may be treated using this process.

Combined-sewer discharges, where separation is not feasible or until it is provided, may be amenable to treatment in this manner. Due to the dilution effect of the low alkalinity stormwater, there should be even more areas of the country where this type treatment is possible than when separated wastewater is treated directly.

Pilot plant studies on a variety of wastewaters are desirable to confirm the findings reported herein, and to examine the suitability of adapting this process to automated-continuous flow situations.

Further investigation of the feasibility of using activated silica of the multinuclear form should be pursued. This appears to be feasible based on the results of the two studies reported in Figures III-5 and V-24. The use of activated silica would therefore be much more attractive, particularly if manufacturers provided solutions which fall in the pH-concentration domain, shown in Figure III-2, designated as stable multinuclear. This would eliminate the need for present day activation practices, including handling of the materials, usually strong acids, required for activation.

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# NOMENCLATURE

| Symbol | Meaning |
|---|---|
| $a$ | Sphere radius (cm) |
| $a_1$ | Ratio of collision radius to the physical radius of a particle |
| $A$ | Net Hamaker constant (ergs) |
| $A_{mm}$ | Hamaker constant of medium particles (ergs) |
| $A_{pm}$ | Hamaker constant of particle and medium. Taken as $(A_{pp} A_{mm})^{\frac{1}{2}}$ (ergs) |
| $A_{pp}$ | Hamakers constant of particles in a vacuum (ergs) |
| $du/dz$ | Velocity gradient ($sec^{-1}$) |
| $D$ | Dielectric constant of the medium (esu/dyne $cm^2$) |
| $D_1$ | Fick's diffusion coefficient ($cm^2$/sec) |
| $D_{11}$ | Mutual diffusion coefficient between two equal-size spheres taken as $2D_1$ ($cm^2$/sec) |
| $D_{11}^*$ | Mutual diffusion coefficient between two equal-size spheres which is a function of interparticle distance due to the mutual viscous interaction of particles ($cm^2$/sec) |
| $D_{t/2}$ | Coagulant dose required to halve the turbidity (mg/l or moles/l) |
| $e$ | Charge on the electron ($4.802 \times 10^{-10}$ esu) |
| $\exp(y)$ | $(2.71828\ldots)^y$ |
| $E_b$, $E_c$ | Energy barrier for conditions b and c respectively (mv) |
| $f$ | Frictional constant of a sphere |

## NOMENCLATURE (continued)

| Symbol | Meaning |
|---|---|
| F | Force of interaction between two particles (dynes) |
| J | Number of particles diffusing through a sphere around the origin in the direction of the stationary central particle (particles/$cm^2$ sec) |
| $J_r$ | Net relative flux of spheres toward the moving central sphere when no barrier to collision exists (particles/$cm^2$sec) |
| $J_s$ | Net relative flux of spheres toward the moving central sphere when a barrier to collision exists (particle/$cm^2$sec) |
| JTU | Jackson Turbidity Units |
|  | Boltzmann constant ($1.38 \times 10^{-16}$ erg/deg) |
| m | An integer used in the Born repulsion term, usually taken between 9 and 12 |
| n | Number of particles per unit volume (particles/$cm^3$) |
| $n_0$ | Initial number of particles per unit volume (particles/$cm^3$) |
| $n_1, n_2, \ldots n_i$ | Number of singlets, doublets,...and i-fold particles per unit volume, respectively (particles/$cm^3$) |
| $n_{0_j}$ | Number of j-kind of ions per unit volume in the bulk solution (ions/$cm^3$) |
| $n'_j$ | Number of atoms per unit volume (atoms/$cm^3$) |
| q | Number of atoms per unit volume (atoms /$cm^3$) |
| R | Distance between centers of two particles at contact (cm) |
| r | Distance from the central particle (cm) |

## NOMENCLATURE (continued

| Symbol | Meaning |
|---|---|
| $t$ | Time (sec) |
| $T$ | Absolute temperature (°K) |
| $T_1$ | Time of coagulation (sec) |
| $V$ | Potential energy of two spheres (ergs) |
| $V_A$ | Potential energy of attraction of two atoms (ergs) |
| $W$ | Fuchs' stability ratio |
| $W_{visc}$ | Fuchs' stability ratio modified to incorporate viscous interaction |
| $x$ | Distance from the flat plate surface (cm) |
| $Z_i$ | Valence of ion |
| $\alpha$ | Aggregation-collision ratio |
| $\alpha_b$ | Born repulsion factor |
| $\alpha_s$ | Smoluchowski's factor to modify the time of coagulation |
| $\beta$ | London atraction constant |
| $\epsilon$ | Size distribution function |
| $\kappa$ | Debye-Huckel Kappa ($cm^{-1}$) |
| $\mu$ | Coefficient of viscosity (poise) |
| $\pi$ | The constant 3.141... |
| $\rho$ | Space charge density ($esu/cm^3$) |
| $\phi$ | Floc volume fraction |
| $\Psi$ | Potential (esu) |
| $\Psi_0$ | Surface potential (esu) |
| $\nabla^2$ | The Laplace operator |

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# I. INTRODUCTION

## Historical Introduction

Chemical coagulation of water for municipal and industrial supply has been studied extensively over the past few decades. Much less attention has been given to coagulation of wastewaters, an integral and primary process in the rapidly developing area of direct physico-chemical treatment of municipal and industrial wastes.

Rudolfs and Gehm (57) first reported the results of an extensive study of chemical treatment of wastewaters in a series of papers in 1936. This study was conducted on wastewaters collected from a number of sewage treatment plants in New Jersey, so selected as to obtain a wide variety of sewage types. The wastewaters were characterized as follows: 1) domestic waste plus effluents from a variety of industries, rather weak and fairly fresh; 2) strictly domestic waste, fresh and somewhat strong; 3) primarily domestic waste, strong, stale and difficult to treat; 4) waste from a large state institution, fresh with average strength; 5) domestic waste plus effluent from a single large manufacturer of soaps, dyes, and alkalies usually stale and of average strength; and

6) domestic waste, stale and of average strength. This series of papers gives a good discussion of the effects of a number of parameters including: pH, turbidity, pre-settling, and type and order of chemical additions.

Results were reported of other early studies of chemical treatment of wastewaters in Atlanta, Georgia (60); Boulder, Colorado (70); Chicago, Illinois (26); Dallas, Texas (65); Grand Rapids, Michigan (16); and Coney Island, New York (56). These and other similar studies resulted in the development of techniques for treatment and some insight into expected performance. Initially chemical treatment was used to provide an effluent superior to that which could be obtained by plain sedimentation alone, and research was directed primarily at solids reduction. During these early periods of formal wastewater treatment development, biological treatment made significant advancement, providing effluents generally superior to those obtained by chemical treatment at significant savings in operating costs. Thus, biological treatment became the favored method and the practice of chemical coagulation fell to disuse.

During the past thirty years, coagulation of wastewaters has been used occasionally, as an intermediate form of treatment and as a temporary measure until adequate biological facilities could be constructed. One example of an intermediate form of treatment was reported in 1951 by Conrad (14). Wooster, Ohio provided plain sedimentation for sewage before discharge to the receiving stream. During low flow and low dissolved oxygen conditions--5 ppm of DO was used as a minimum--chemical treatment was provided to maintain the dissolved oxygen level of the receiving stream. Chlorine was added to the waste at the beginning of a dissolved oxygen decline in the stream to reduce BOD exertion. However, during more severe periods of oxygen deficiency, ferric chloride was used in conjunction with calcium oxide. The benefits claimed using the ferric chloride-calcium oxide treatment were reported in terms of averages over a several year period and are as follows: 1) suspended solids reduction was increased from 65.1 to 83.2%, 2) BOD reduction was increased from 39.8 to 62.0%, and 3) settleable solids reduction was increased from 90.6 to 97.0%. The chemicals were normally applied to the raw wastewater and settled in the primary tank. A number of studies were run where the chemicals were added after primary settling, followed by flocculation, and secondary sedimentation. This procedure resulted in no significant increase in solids or BOD reduction over that obtained by direct addition of chemical to the raw sewage, required twice the number of settling tanks, and therefore was not used routinely.

Certain industrial wastewaters are amenable to coagulation. Paper mill wastewaters, for example, are often treated by chemical coagulation followed by sedimentation (53, 11), and Hutchinson (30) has demonstrated that coagulation followed by air floatation is effective for such wastewaters. Hart (25) summarized the experience and types of chemicals frequently used in the chemical clarification of oil bearing wastewaters. Food processing wastes constitute another category of wastewaters frequently treated by chemical clarification. Webster (76), for example, reported the results of pilot-plant studies on treatment of a variety of vegetable wastes and found chemical coagulation effective in removing suspended solids (75 to 83% reduction), although BOD reduction was not found to be as complete (15 to 42% reduction). The relatively low BOD removal was attributed to the high percentage of total solids which were dissolved (90%) and apparently not removed to any significant extent.

Recent interests in removing phosphates from conventionally treated wastewaters and in the direct physicochemical treatment of wastes has rekindled interest in chemical precipitation and coagulation processes. An ever increasing number of wastewater treatment plants are including chemical precipitation of phosphates. Nilsson (44) in a recent article discussed the increased practice of chemical precipitation of phosphates in Sweden. Less than one year ago, Schuessler (58) discussed the results of a number of studies conducted by the Dow Chemical Company on the removal of phosphates from municipal sewages in the United States using metal coagulants and organic polyelectrolytes. In most of these cases chemical precipitation of phosphates occurs in the primary settling tank with chemical additions being made to the raw wastewater. Significant improvement, as would reasonably be expected, was noted in the removal of BOD and suspended solids in the primary tank in addition to the removal of phosphates.

Increased rates of eutrophication and other forms of degradation of receiving waters and the increased reuse of water both directly and indirectly have clearly demonstrated the need for some form of treatment superior to conventional biological treatment. Chemical coagulation could well play a key role in this higher form of treatment. Perhaps, following conventional biological treatment or possibly eliminating biological treatment when used with some other form of treatment such as adsorption on carbon. The feasibility of using coagulation-sedimentation followed by adsorption has been demonstrated and shown to have economic advantages over biological treatment in many instances, and over tertiary treatment of biological effluents where higher degrees of treatment are desired (74).

Accompanying any significant increase in completeness of treatment, will most likely be an increase in direct water reuse. A recent study (63) to improve the quality of a bleached craft effluent led to this conclusion. It

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This report is being made available in its present form with the hope it will be of sufficient value to justify its announcement and distribution.

adsorption on carbon, filtration or other advanced forms of waste treatment become more attractive than biological treatment for producing a nearly pure reusable water. A second area of application is in the chemical treatment of urban storm runoff. Urban runoffs contain significant amounts of pollutants, as has been demonstrated in a number of studies. For example, Burm, Krawczyk, and Harlow (12) summarized the findings of several studies and reported findings for a study conducted in Detroit and Ann Arbor, Michigan. In all these studies significant pollutants were found in storm runoff, resulting in pollution of receiving streams. It may be necessary to treat these waters, especially after municipal and industrial wastes are treated to higher degrees, to adequately protect receiving waters from eutrophication and other forms of degradation, and to restore and preserve them for higher uses. The American Chemical Society (2) in its report "Cleaning Our Environment--The Chemical Basis For Action" recognized the need for ultimately treating urban storm runoff in their Recommendation W9:

> Systematic studies should be undertaken of the quality of urban storm waters to provide a sound base for assessing alternative means of treatment.

Chemical treatment, subject to relatively ready automation and control, may well prove to be most suitable for this type of waste (i.e. intermittent and highly variable flows), especially if sedimentation or storm water storage is to be provided as is presently the case in a number of locations (52). Treatment by chemical coagulation may provide an alternative to separation of combined sewers, particularly in areas where treatment of storm or urban runoff is planned.

## Preliminary Considerations

Based on the anticipated expansion in the applications of chemical coagulation in wastewater treatment, it appeared desirable to attempt to refine the technology thereof, most of which had been developed several decades ago and under less rigid treatment requirements. A review of the literature indicated that metal coagulants alone would probably not provide the degree of treatment desired in all cases. For this study it was decided to examine in detail one reagent, activated silica, as it might be used as an adjunct to metal-ion coagulants for waste treatment. The reasons for selecting activated silica include: 1) there is a long history of its successful use as a coagulant aid in potable water treatment; 2) sodium silicate, from which activated silica is prepared, is available in large quantities at reasonable prices; 3) equipment is currently available to prepare and feed activated silica in sufficiently large capacities; and 4) because silica is a natural constituent of most waters, its use involves little if any danger of introducing a foreign material to the treated water.

Dating to its use by Baylis (4) and Graf and Schworm (20), activated silica has been used primarily in conjunction with alum to treat surface water supplies. The use of activated silica with the metal coagulant iron is uncommon. Wheaton and Walker (77) reported experimental observations that indicated there seems to be no advantage obtained using activated silica with ferric coagulants. Black (8) and others (9, 51, 54,) reported alum could be replaced in part or total by activated silica for removal of calcium carbonate precipitated during lime softening of water. McDowell (40) also reported that in England activated silica was found to be a valuable coagulant in the lime and lime-soda softening treatment of water.

Preliminary coagulation studies, conducted in accordance with procedures described in a later chapter, in which activated silica was used in conjunction with alum to coagulate a 5-micron Min-U-Sil silica suspension, a product of Pennsylvania Glass Sand Corporation, Pittsburg,--a typical test dispersion for evaluation of coagulation effects--are shown in Figure I-1. Results are expressed as the amount of alum required to halve the initial turbidity, $D_{t/2}$--a technique used by Packham (48) for presenting coagulation data--as a function of pH for several concentrations of activated silica. It was found possible to reduce alum requirements in the acid zone with addition of low quantities of silica (1 to 2 mg/1

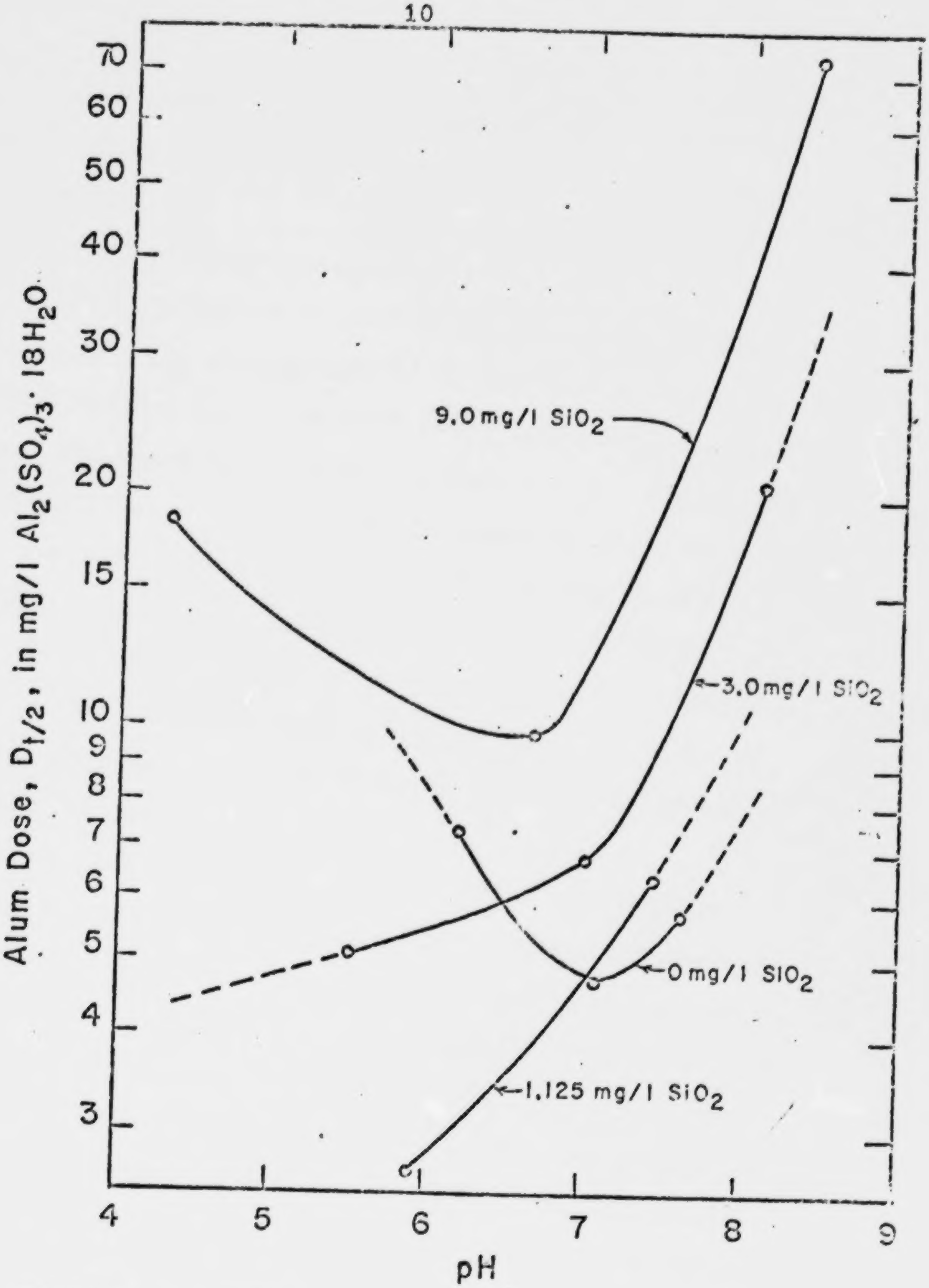

FIGURE I-1. VARIATION OF THE COAGULANT DOSE REQUIRED TO HALVE THE TURBIDITY ($D_{t/2}$) of 75 mg/1 5-MICRON MIN-U-SIL AS A FUNCTION OF pH AND ACTIVATED SILICA DOSE.

Residual pH held within plus or minus 0.2 pH units by varying the concentration of sulfuric acid with either sodium bicarbonate or sodium carbonate. These pH adjustments were made before treatment with calcium hydroxide.

$SiO_2$). The activated silica appeared to have detrimental effects at higher dosages and higher pH, causing increases in alum requirement.

Additional preliminary coagulation studies were performed using activated silica in conjunction with lime to clarify 150 mg/l suspensions of bentonite--another common test dispersion--in a $10^{-3}$ molar sodium bicarbonate solution. The results are shown in Figure I-2. Significant reduction in lime dosage required to reach an acceptable effluent quality is noted when activated silica is used under these conditions. Lime, in addition to being an effective reagent for removing phosphates, has the advantage of adding no anions other than hydroxide and carry-over of calcium results only in an increase of a naturally occuring substance in the treated water.

Based partially on the results of these preliminary studies and the literature review it was decided to conduct a practical investigation focused on the potential use of activated silica in conjunction with lime. A summary of the current status of theories of coagulation-flocculation was prepared based on a literature study. It was recognized that the synthetic and natural systems of concern in this study, for the most part, fall well outside the limitations imposed by these theories. This theoretical summary was intended to be used to assist in interpreting observed experimental results, and not for the purpose of experimentally verifying theory.

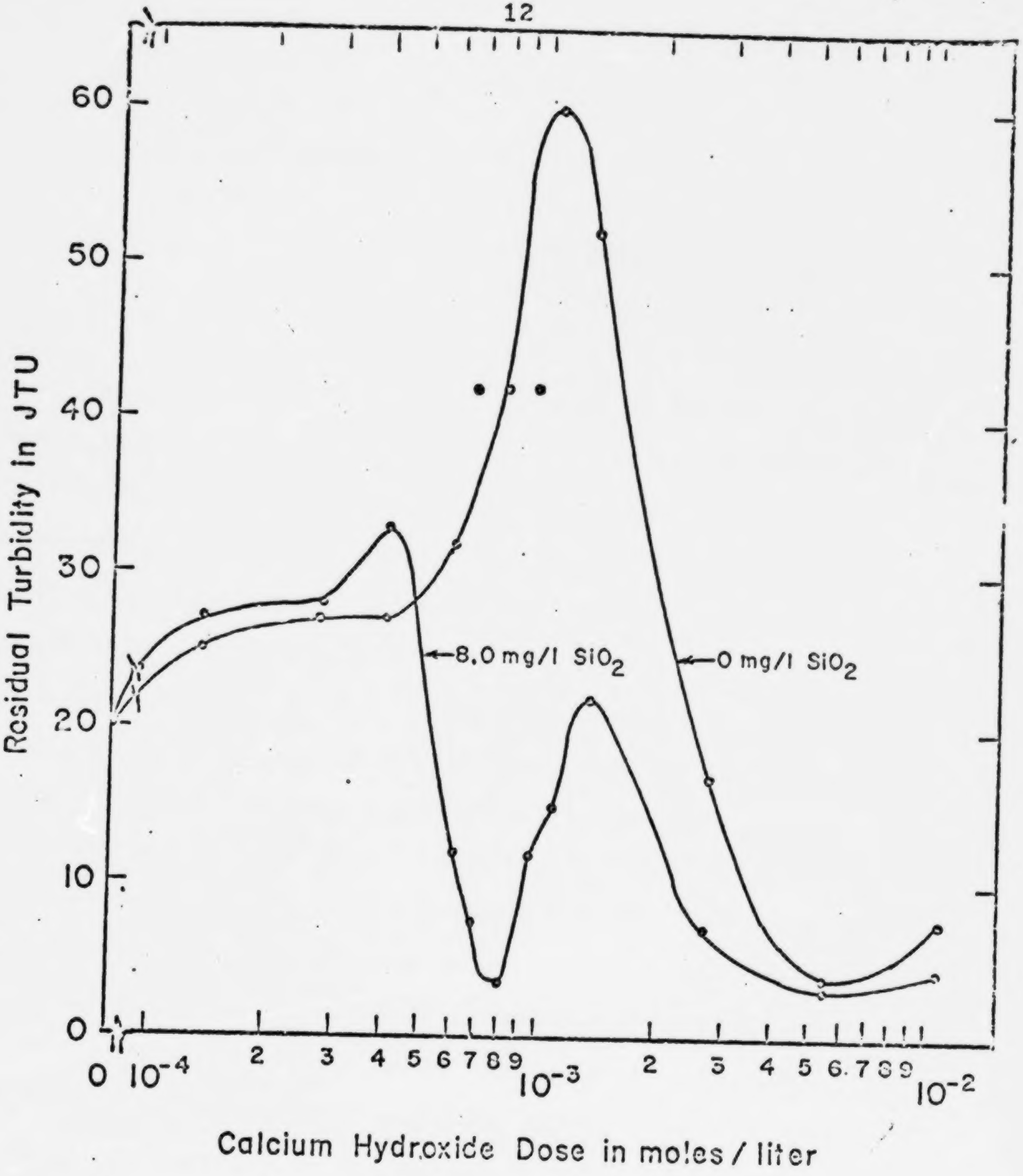

FIGURE I-2. EFFECT OF ACTIVATED SILICA ON CLARIFICATION OF A SUSPENSION OF 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE USING CALCIUM HYDROXIDE.

# II. COAGULATION THEORY

## Introduction

Wastewaters contain a wide variety of substances both organic and inorganic in nature. It is customary to broadly classify these substances in terms of physical dimensions. Particles larger than one micron generally settle on standing and are usually referred to as suspended substances. Particles less than one micron, but larger than dissolved substances (i.e. about ten angstroms) are referred to as colloidal substances. Colloidal particles have the distinguishing characteristic of a very high surface area to mass ratio. Therefore, the forces associated with surfaces become more important than the influence of gravity on the relatively small masses. This surface area to mass consideration is frequently emphasized by the comparisons shown in Table II-1. In general, the particles in a dispersed colloidal system will not settle due to gravity, cannot be removed by ordinary filtration, and are not visible microscopically except as specks of light in a Tyndall beam.

TABLE II-1

EFFECT OF DECREASING SIZE ON SURFACE AREA

| No. of Equal-Sized Cubes Cut from a 10-mm Cube | Size of Each Cube in mm | Order of Size | Total Surface Area in $mm^3$ |
|---|---|---|---|
| 1 | 10 | Gravel | $6 \times 10^2$ |
| $10^3$ | 1 | Coarse Sand | $6 \times 10^3$ |
| $10^6$ | 0.1 | Fine Sand | $6 \times 10^4$ |
| $10^9$ | 0.01 | Silt | $6 \times 10^5$ |
| $10^{12}$ | 0.001(1μ) | Bacteria | $6 \times 10^6$ |
| $10^{15}$ | 0.0001 | Large Colloid | $6 \times 10^7$ |
| $10^{18}$ | 0.00001 | Colloid | $6 \times 10^8$ |
| $10^{21}$ | 0.000001(10Å) | Small Colloid | $6 \times 10^9$ |

## Colloidal Stability

In general, the stability of colloids in water, or their tendency to resist separation by settling due to gravity, may be accounted for by three factors: 1) electrostatic repulsion, 2) hydration, and 3) entropic repulsion, or a mixture of these. These factors are discussed here in a qualitative fashion and in more detail in the next section.

Hydration is due to water molecules becoming attached to the surface of the colloidal particles, rendering the latter more water-like and capable of resisting separation from the aqueous phase. This attraction is due to the polar nature of water molecules. Water in the absence of ion impurities or other particles tends to be arranged in clusters of molecules of more or less definite crystalline arrangement. The hydrogen atoms of one molecule are aligned toward the oxygen atoms of another water molecule. The oxygen atoms surround themselves in a tetrahedral configuration with four hydrogen atoms, and as water molecules move hydrogen atoms undergo frequent exchange. When ions or charged colloidal particles are immersed in water, there is a partial breakdown of the water clusters with the water molecules moving around the charge particles forming a hydrated layer or solvation shell. This hydrated layer protects charged particles from contact with other such particles and may result in a relatively stable system.

Steric or entropic repulsion may exist due to the adsorption of polymeric substances on the surfaces of the colloidal particles. When two particles with adsorbed polymers approach one another, the loss of configurational freedom of the polymers due to interpenetration or compression leads to a decrease in configurational entropy of the polymers and an increase in free energy of the system, thus repulsion between the approaching particles.

This repulsion due to adsorbed polymers may prevent colloids from coming into contact, thus stabilizing the system.

Overbeek (46) considers the interaction of colloidal particles to consist of two components. One, repulsion due to the electrical double layer and the other the general London-van der Waals attraction. Stability then is a measure of the velocity of coagulation. A stable system is one which has an immeasurably slow velocity and an unstable system is one which coagulates in a relatively short period of time. That is to say, in an unstable system attraction dominates causing colloidal particles to come together at a relatively high rate, and grow in size sufficiently large to settle under the influence of gravity. In a stable system, repulsion dominates and colloidal particles do not come together at a significantly high rate, thus the particles remain in suspension.

It has often been observed that colloidal particles move in an electrical field. This indicates they must carry a charge on their surfaces. The origin of this charge may result from one of these four processes: 1) preferential adsorption of ionic surfactants on their surfaces; 2) adsorption of potential-determining ions from the liquid; 3) dissociation of surface groups; and 4) excess of charge in the interior of the particles, possibly due to crystal lattice imperfections. Electroneutrality demands a particle plus its immediate surroundings bear no net charge. Therefore charged particles immersed in an aqueous phase must be accompanied by species of equal but opposite or counter-charge within the solution. These charges, surface-charge and counter-charge, together form the electrical double layer. When two particles, each having an electrical double layer, approach one another, their double layers overlap, causing a disturbance which results in an increase in potential energy of repulsion. Unless the particles are capable of overcoming the resulting electrostatic repulsive force, they are repelled and the system is considered stable due to electrostatic repulsion.

The other type of electrical repulsion which may be encountered is the quite general repulsion that arises if any two atoms are brought too close together. This repulsion is due basically to the reluctance of the electron clouds of the two atoms to overlap each other. Therefore, it is very much dependent on separation and important only for distances of the order of atomic dimensions. Since interaction of colloids occurs at much greater than atomic dimensions, these electrical forces will be insignificant when compared to those due to the electrical double layer overlap in colloidal systems.

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## Colloid Destabilization

Colloid destabilization is a process of overcoming the factors responsible for colloid stability. Once these factors are overcome the particles may join together and grow sufficiently large to settle under the influence of gravity in a reasonable period of time.

The terms coagulation and flocculation are often used interchangeably to mean the joining together of colloidal particles to form particles sufficiently large to settle under the influence of gravity. LaMer (35) makes a useful distinction between the two terms. Coagulation means driving together due to the effect of salts on the colloidal dispersion. Here the electrical layer is compressed causing a reduction in the electrostatic repulsion and subsequently the joining together of particles. The main destabilization effect being a reduction of ionic forces of repulsion. The resulting floc is usually relatively small and dense. Flocculation refers to chemical bridging or physical enmeshment of particles. The main driving force being London-van der Waals dispersion force and the resulting floc usually is relatively large and porous.

## Kinetics of Coagulation.

The kinetics of coagulation may be described by

Smoluchowski's theory of rapid coagulation, which assumes a dilute solution of solid, equal-size spheres in a liquid. The spheres are in Brownian motion and no barrier to collision exists. Smoluchowski's model predicts change in concentration of singlets, doublets, and other size groups of particles with respect to time.

Overbeek (47) has given a convenient summary of Smoluchowski's work which leads to the following set of equations:

$$n_1 = \frac{n_0}{(1+t/T_1)^2} \qquad \text{(II-1)}$$

$$n_2 = \frac{n_0(t/T_1)}{(1+t/T_1)^3} \qquad \text{(II-2)}$$

$$n_i = \frac{n_0(t/T_1)^{i-1}}{(1+t/T_1)^{i+1}} \qquad \text{(II-3)}$$

where $n_0$ is the initial number of particles per unit volume; $n_1$, $n_2$, and $n_i$ are the number of singlets, doublets, and i-fold particles per unit volume, respectively, at any time, t; and $T_1$ is a collection of constants called the time of coagulation which equals the time in which the number of particles is halved. The above set of equations is illustrated in Figure II-1 taken from Overbeek's (47) summary.

The above equations are based on the assumption of

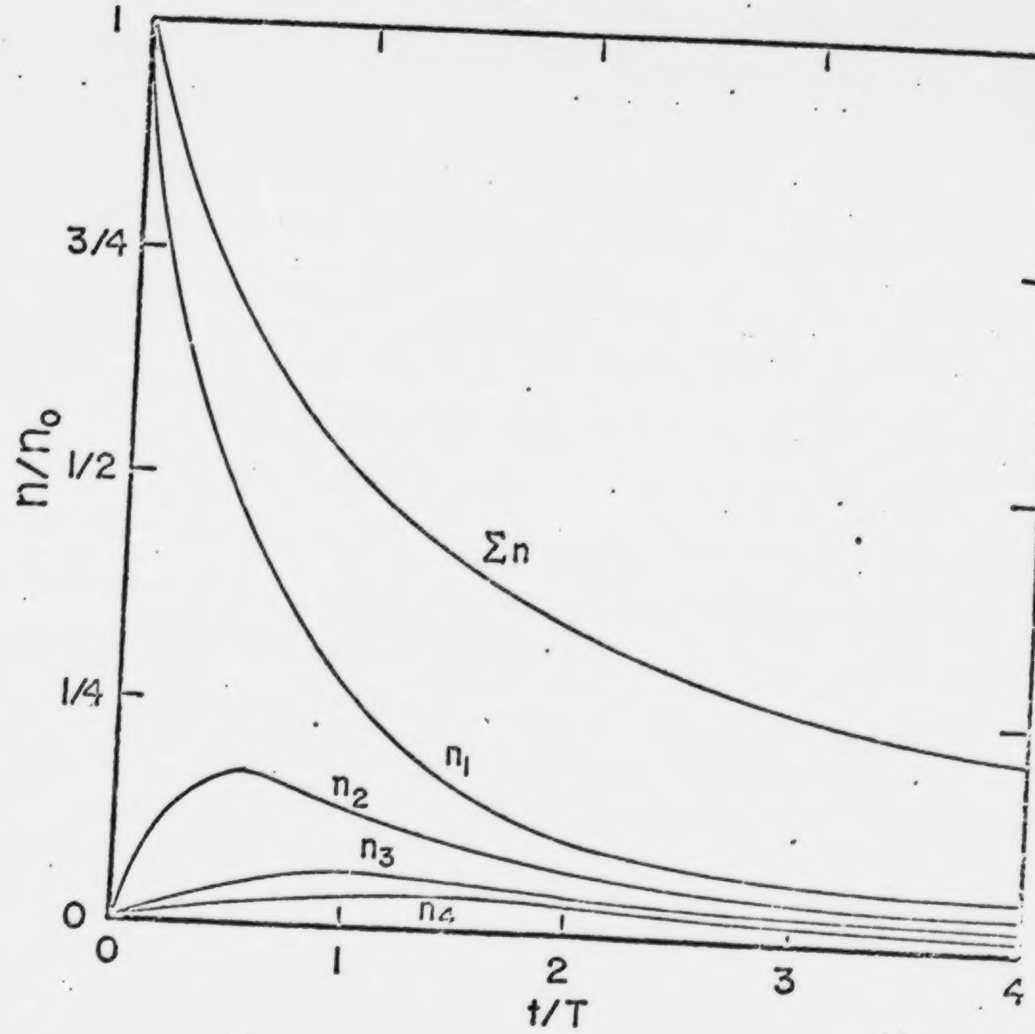

FIGURE II-1. PARTICLE SIZE DISTRIBUTION AS A FUNCTION OF TIME ACCORDING TO SMOLUCHOWSKI'S THEORY OF RAPID COAGULATION.

Total number of particles, singlets, and doublets, are represented by n, $n_1$, $n_2$, etc., respectively, at any time, t; $n_0$ represents initial number of particles; and T represents time of coagulation which equals the time required to halve the total number of particles. Source: Reference 47.

rapid coagulation which means, of the two factors responsible for the rate of coagulation, only Brownian motion is significant. The other factor, the repulsive force, is neglected. It is further assumed in this model that all particles approach one another unhindered and all contacts result in irreversible combination. This would be approached in a real system containing high electrolyte concentration, where repulsion is reduced to a negligible level.

In most systems, however, the repulsion energy is significant and has been accounted for by one of two assumptions. First, as a consequence of the partial effectiveness of collision Smoluchowski (47) proposed a theory of slow coagulation by introducing a factor which modifies the time of coagulation, $T_1$, as follows:

$$T_1 = \frac{1}{4\pi D_1 R n_0}, \text{ for rapid coagulation, and} \qquad \text{(II-4)}$$

$$T_1 = \frac{1}{4\pi D_1 R n_0 \alpha_s}, \text{ for slow coagulation} \qquad \text{(II-5)}$$

where $D_1$ is Fick's diffusion coefficient of the primary particle, R is the distance between centers of the two particles at contact, $n_0$ is the initial number of particles per unit volume, and $\alpha_s$ is the factor used to modify the time of coagulation. The factor $\alpha_s$, unfortunately has no theoretical connection to the magnitude of the repulsion energy. The second approach proposed by Fuchs (47) modifies Fick's diffusion equation to include diffusion in a field of force. Fuchs introduced the stability ratio, W, which is the ratio of the rates of rapid coagulation and slow coagulation. This ratio and recent modification are developed in the following paragraphs.

Rapid coagulation, based on steady-state diffusion control, is given by Fick's diffusion equation as follows:

$$J = 4\pi r^2 D_1 \frac{\partial n}{\partial r} \qquad \text{(II-6)}$$

where J is the number of particles diffusing through a sphere around the origin in the direction of the stationary central particle, n is the number of particles per unit volume, and r is the distance from the central particle. The solution of Equation II-6 satisfying the boundary conditions:

$$n = n_0 \text{ for } r = \infty$$

$$n = 0 \text{ for } r = 2a$$

is as follows:

$$J = 8\pi D_1 a n_0 \qquad \text{(II-7)}$$

where a is the radius of the sphere, assuming equal-size spheres. If the central particle is also subject to Brownian motion, and the motion of the two equal-size spheres is assumed to be completely independent of each other, the mutual diffusion coefficient between the two spheres may be taken as: $D_{11} = 2D_1$, the sum of the single sphere diffusion coefficients. Equation II-7, therefore becomes:

$$J_r = 8\pi D_{11} a n_0 \qquad \text{(II-8)}$$

where $J_r$ is the net relative flux of spheres toward the central moving sphere when no barrier to collision exists.

Slow coagulation, based on the above assumptions except a barrier to collision exists, is given by diffusion in a field of force. The expression, as proposed by Fuchs, is as follows:

$$J = 4\pi r^2 \left(D_1 \frac{\partial n}{\partial r} + \frac{n}{f} \frac{\partial V}{\partial r}\right) \qquad \text{(II-9)}$$

where V is the potential energy of two spheres, f is the frictional constant of a sphere ($=6\pi\mu a$), and $\mu$ is the coefficient of viscosity. When the central sphere is free to move, $D_1$ is replaced by $D_{11}$ as was done above. Einstein's general relationship between f and $D_{11}$, $fD_{11} = kT$; and the force of interaction, F, which is equal to the negative gradient potential of interaction, $F = -\partial V/\partial r$, are used to modify Equation II-9 as follows:

$$J_s = 4\pi r^2 \left(D_{11} \frac{\partial n}{\partial r} - \frac{nD_{11}}{kT} F\right) \qquad \text{(II-10)}$$

where $J_s$ is the net relative flux of spheres toward the central moving sphere when a barrier to collision exists, k is the Boltzmann constant, and T is the absolute temperature. Equation II-10 may be rearranged as follows:

$$\frac{\partial n}{\partial r} - \frac{Fn}{kT} = \frac{J_s}{4\pi r^2 D_{11}} \qquad \text{(II-11)}$$

The solution of this non-exact, first order, linear differential equation using the boundary conditions:

$n = n_0$ and $V = 0$ for $r = \infty$

$n = 0$ and $V = -\infty$ for $r = 2a$

and the integrating factor:

$$\exp\left(-\int \frac{F}{kT}\,dr\right) = \exp\left(\frac{V}{kT}\right) \qquad \text{(II-12)}$$

is as follows:

$$J_s = \frac{4\pi D_{11} n_0}{\int_{2a}^{\infty} \exp\left(\frac{V}{kT}\right)\frac{\partial r}{r^2}} \qquad \text{(II-13)}$$

The stability ratio, W, used by Fuchs is by definition:

$$W = J_r/J_s \qquad \text{(II-14)}$$

Therefore, using Equations II-8 and II-13, the stability ratio is as follows:

$$W = 2a\int_{2a}^{\infty} \exp\left(\frac{V}{kT}\right)\frac{\partial r}{r^2} \qquad \text{(II-15)}$$

The assumption that the two equal-size spheres move completely independent of one another leads to difficulty when they approach one another. As they approach, hydrodynamic interaction diminishes the coagulation rate (27). In the development of Equation II-15 it has been assumed that the mutual diffusion coefficients between two spheres, $D_{11}$, is equal to the sum of the single sphere diffusion coefficients ($D_{11} = 2D_1$). Spielman (64) has proposed a modification to Equation II-15 by introducing a mutual diffusion coefficient between two spheres, $D_{11}^*$, which is a function of interparticle distance due to the mutual viscous interaction of particles. When the spheres are infinitely far apart $D_{11}^* = D_{11}$, but $D_{11}^*$ decreases with decreasing interparticle distance, and approaches zero as the interparticle distance approaches zero compared to the radius of the particle. Therefore at the limits, the ratio $D_{11}/D_{11}^*$ approaches unity when interparticle distance approaches infinity and $D_{11}/D_{11}^*$ approaches infinity when interparticle distance approaches zero. The stability ratio modified to incorporate viscous interaction, $W_{visc}$, is as follows:

$$W_{visc} = 2a \int_{2a}^{\infty} \left(\frac{D_{11}}{D_{11}^*}\right) \exp\left(\frac{V}{kT}\right) \frac{\partial r}{r^2} \qquad \text{(II-16)}$$

The above model for describing the kinetics of coagulation is often referred to as perikinetic flocculation or perikinetic coagulation, meaning collisions are promoted primarily by Brownian motion. This is the case during the first stages when particles are still relatively small. As the particles become large however, Brownian motion becomes less significant until finally particle collisions are governed primarily by velocity gradients resulting from mixing. This condition is referred to as orthokinetic flocculation. The theoretical development of perikinetic flocculation, as noted above, is very restrictive and experimental verfication has been limited to the very early stages of particle growth. Once the system has reached the point where Brownian motion is no longer the dominant collision producing factor, and in natural waters and wastewaters which are already a potpourri of substances, theoretical development is practically hopeless. Harris, et al (24) recently attacked this very difficult problem and developed a rate equation for orthokinetic flocculation, which they hoped would be useful in design of water treatment plant flocculators. Their rate equation is as follows:

$$\frac{dn_1}{dt} = -\frac{\alpha\epsilon {a_1}^3}{\pi}\frac{du}{dz}\phi n_1 \qquad \text{(II-17)}$$

where $n_1$ is the number of primary particles per unit volume at time, t; $a_1$ is the ratio of the collision radius to the physical radius of the particle; $\phi$ is the floc volume fraction or volume of floc per unit volume of fluid; $\epsilon$ is defined as the size distribution function and may be considered a measure of the degree to which the size distribution deviates from one of all primary particles (i.e. a measure of polydispersity); $\alpha$ is the aggregation-collision ratio and is a measure of the primary particle stability; and du/dz is the velocity gradient. It is obvious from an examination of the factors which are included in the above rate equation that orthokinetic flocculation theory will remain a challenge, particularly as applied to wastewater treatment.

Energetics of Coagulation.

The energetics of particle-particle interaction may be represented by total potential energy of interaction, which is considered to be the sum of the potential energy of repulsion and potential energy of attraction.

The repulsion part is due to the existence of the electrical double layer. A classical treatment of the single flat electrical double layer is based on the Gouy-Chapman model. The six assumptions for this model are: 1) surface charges are uniformly distributed to produce a smeared out field on the surface; 2) ions are point charges and occupy no volume; 3) solvents affect the electrical double layer through their dielectric constant; 4) no irreversible adsorption is permitted; 5) the preferential distribution of counter ions follows the Boltzmann distribution law, which states that the probablity of finding an ion at some particular point will be proportional to the Boltzmann factor,

$$\exp(-Z_1 e \Psi/kT) \qquad \text{(II-18)}$$

where $Z_1$ is the valence of the ion, $e$ is the charge on the electron, $\Psi$ is the potential, $k$ is the Boltzmann constant, and $T$ is the temperature, thus:

$$n_j = n_{0_j} \exp(-Z_1 e \Psi / kT) \qquad \text{(II-19)}$$

where $n_j$ is the number of j-kind of ions per unit volume at a point where the potential is $\Psi$, and $n_{0_j}$ is the number of j-kind of ions per unit volume in the bulk solution; and 6) Poisson's equation applies, which is as follows:

$$\nabla^2 \Psi = -4\pi \rho / D \qquad \text{(II-20)}$$

where $\rho$, is the space charge density at any point, D is the dielectric constant of the medium, and $\nabla^2$ is the LaPlace operator which is used to relate the potential distribution to the space charge density of the counter ions. In the case of a flat plate the potential, $\Psi$, varies with distance from the plate's surface, x, according to the relationship found in most elementary texts on this subject:

$$\Psi = \Psi_0 \exp(-\kappa x) \qquad \text{(II-21)}$$

where $\Psi_0$ is the surface potential and $\Psi$ is the Debye-Hückel Kappa defined by,

$$\kappa^2 = \frac{8\pi n_0 e^2 Z_1{}^2}{\epsilon kT}\,. \qquad \text{(II-22)}$$

In arriving at this relationship for potential, the Debye-Hückel linear approximation was made, which is valid when $Z_1 e \Psi_0 / kT << 1$ and $Z_1 e \Psi / kT << 1$. The Debye-Hückel Kappa is also often used to approximate the thickness of the electrical double layer, $1/\kappa$.

The validity of the assumption of no volume occupied by ions decreases near the surface, especially when x is small and $\Psi_0$ is large. Under these conditions, the Stern treatment provides an important correction to the double layer theory by correcting for the finite dimensions of the ions. This is accomplished by dividing the region near the surface into two parts, the first called the Stern layer, consists of a layer of ions adsorbed at the surface and the second consisting of a diffuse layer according to the Gouy-Chapman model. In addition to these layers, other divisions in the electrical double layer have been proposed (1, 59). An illustration after Sennett and Oliver (59) which is an attempt to better define the region near the particle surface is shown in Figure II-2. A discussion of the nature of the different parts as shown in this figure, is as follows.

1. Potential-determining layers consist essentially of ions or surface groups identified with the solid phase. For example, chloride ions from solution which are adsorbed on the surface of the particle would then mingle with other chloride ions from the particle and become indistinguishable from them. These may then be thought of as absorbed ions or an adsorbed layer as shown in the

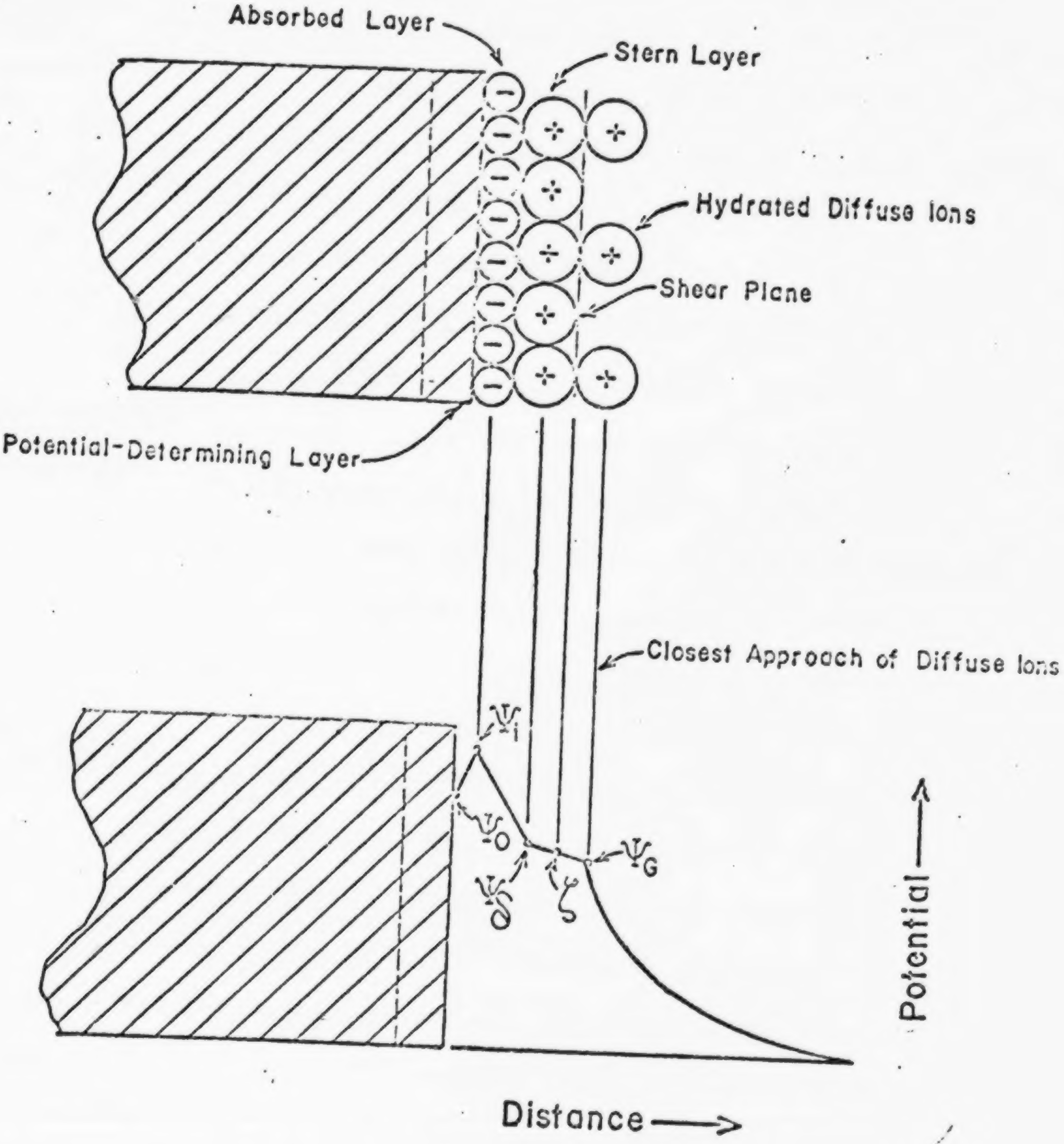
Absorbed Layer
Stern Layer
Hydrated Diffuse Ions
Shear Plane
Potential-Determining Layer
Closest Approach of Diffuse Ions
$\Psi_i$
$\Psi_O$
$\Psi_\delta$
$\zeta$
$\Psi_G$
Potential
Distance

FIGURE II-2. A MODEL OF THE ELECTRICAL DOUBLE LAYER.

Potentials are represented as follows: $\Psi_O$, surface potential; $\Psi_i$, potential of absorbed layer; $\Psi_\delta$, potential of the Stern layer; $\zeta$, zeta potential or potential at shear plane; and $\Psi_G$, potential at the limit of the Gouy-Chapman Model which is located one-half the diameter of a hydrated diffuse ion from the Stern layer. Source: Reference 59.

illustration. This layer, which is identified with the solid phase but is unlike the interior bulk solid phase, may be considered as the potential-determining layer.

2. Stern layers may be considered as second layers of at least partially solvated ions held fairly strongly and being rather immobile.
3. Shear planes would occur at that point in the diffuse layer where liquid shear is resisted and the potential at these planes is known as the zeta potential. It may coincide with the Stern layer or more likely be beyond it since immobility is primarily a property of the solvent, therefore need not coincide with the Stern layer boundary.

Electrostatic repulsion of overlapping electrical double layers may be quantified using the theory proposed by Derjaguin and Landau (Russian) (18) and independently by Verwey and Overbeek (Dutch) (71) and commonly referred to as the DLVO Theory. The DLVO Theory provides a means of determining the electrostatic repulsion between plates, plates and spheres, and spheres based on either an assumed constant surface potential or an assumed constant surface charge density. A discussion of the comparison of these two assumptions is given by Jones and Lavine (31).

The electrical forces responsible for attraction are the dispersion forces known as London-van der Waals forces. These forces may be viewed as the attraction of a positive nucleus for electrons beyond its own electron sphere. London (38) presented a quantum mechanics consideration of this attractive force. Since a particle cannot lie absolutely at rest according to quantum mechanics, an instantaneous view of a molecule would show various configurations of nuclei and electrons resulting in a general dipole moment. These quickly varying dipoles produce an electrical field and induce dipoles on other neighboring molecules resulting in attraction. These forces are very short range between atoms but in colloidal particles or macromolecules these dispersion forces can be long range due to the additivity of the dispersion effect of all the atoms (between atoms in both particles, between atoms within each particle, between atoms in the particle with the surrounding medium, and between atoms in the surrounding medium). London's basic relationship for potential energy of attraction between two atoms is given as:

$$V_A = \frac{-\beta}{r^6} + \frac{\alpha_b}{r^m} \qquad \text{(II-23)}$$

where $\beta$ is the London attraction constant, $r$ is the interatomic distance, and $\alpha_b/r^m$ is the Born repulsion term in which $\alpha_b$ is the Born repulsion factor and m is an integer usually taken between 9 and 12. When r approaches zero the Born repulsion part is greater due to the overlap of the electron clouds. However, when r is much greater than zero the Born repulsion term becomes less important and the potential energy of attraction approaches:

$$V_A = - \frac{\beta}{r^6}. \qquad \text{(II-24)}$$

From this basic relationship the potential energy of attraction between an atom and an infinitely long thin plate may be computed by summing the attraction between all the atoms of the plate with a single atom. Then, this concept may be expanded to two plates by integration, a plate and a sphere, and finally two spheres. The development of these relationships is not included herein, but may be found in a number of references, for example (1, 46).

In the development of the potential energy of attraction, Hamaker (22) introduced a constant,

$$A = q^2 \pi^2 \beta, \qquad \text{(II-24)}$$

where A is Hamaker's constant, q is the number of atoms per cubic centimeter, and β is London's constant introduced earlier.

As shown above, the London constant, β, is important when considering the potential energy of attraction between atoms. Hamaker's constant, A, similarly is important when considering the potential energy of attraction between colloids or macromolecules. It treats the attraction in a composite way rather than as a multi-bodied problem. The net Hamaker constant consists of the Hamaker constants of the parts as follows:

$$A = A_{pp} + A_{mm} - 2A_{pm} \qquad \text{(II-26)}$$

where A is the net Hamaker constant, $A_{pp}$ is the Hamaker constant of particles in a vacuum, $A_{mm}$ is the Hamaker constant of the medium particles, and $A_{pm}$ is the Hamaker constant of particle and medium taken as $(A_{mm}\ A_{pp})^{\frac{1}{2}}$.

The total potential energy of interaction is the sum of the repulsion and the attraction parts discussed above. Three typical plottings of the total potential energy are shown in Figure II-3. Curve A represents the case where repulsion is negligible and attraction occurs at all interparticle distances. Kinetically this would be rapid coagulation as no barrier to collision is present. Curve B represents the case where repulsion dominates, yeilding a high energy barrier, $E_b$, which would prevent two particles from colliding. This system is considered to be stable. Curve C is the intermediate case, where the energy barrier, $E_c$, is sufficient to prevent low energy collisions from overcoming the barrier but not sufficient

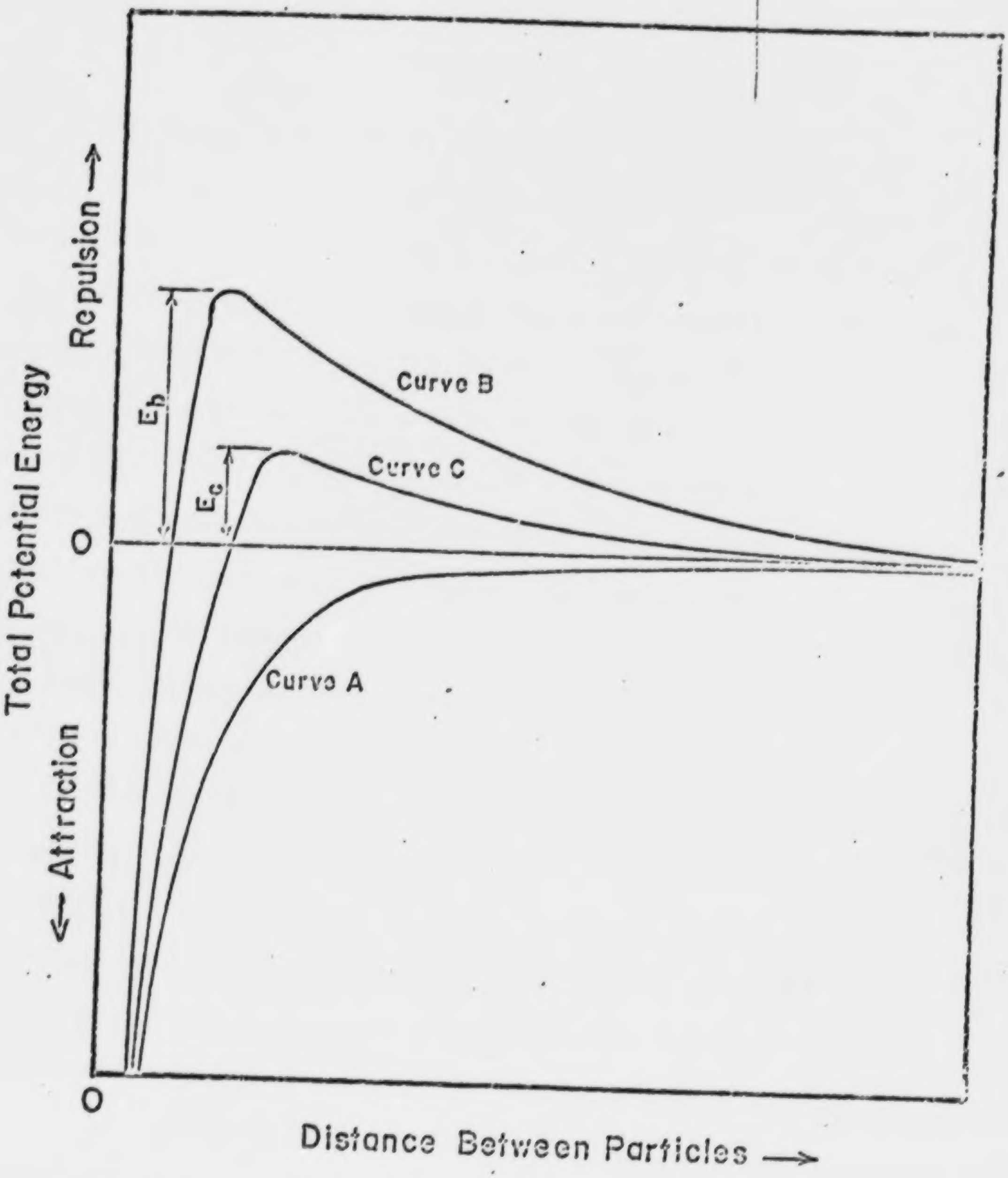

FIGURE II-3. TOTAL POTENTIAL ENERGY OF INTERACTION BETWEEN TWO PARTICLES.

to prevent high energy collisions from overcoming the energy barrier. This would be an example of slow coagulation and the rate would be a function of the proportion of the particle-particle collisions which contain sufficient energy to overcome the energy barrier, $E_c$.

The above discussion, based on the DLVO Theory, ignores the stability promoting or opposing action of polymers, and therefore is applicable only when no polymeric adsorption is involved. Polymers, when adsorbed on colloids, cause three principal observable effects. These are: 1) protection, where the polymers stabilize disperse systems against coagulation; 2) sensitization, where the adsorbed polymers promote coagulation with the addition of low concentrations of salt; and 3) adsorption coagulation, which is seen with low polymer concentrations and yeilds coagulation without the aid of salts. The mechanisms by which adsorbed polymers effect the stability of dispersed systems are: 1) when polymers are charged, they produce an increased electrical repulsion; 2) the polymers can produce Vold's effect (72), which is a reduction of potential energy of attraction between two particles caused by a change in the net Hamaker's constant when the Hamaker's constant of the polymer is sufficiently different from those of the colloidal particle and medium; 3) two particles with low polymer surface coverage may flocculate due to adsorption of polymer segments from one particle to the other forming bridges (LaMer's theory of flocculation 35); 4) if polymers are charged and able to neutralize part of the surface charge on the particle, coagulation is promoted and will be highly sensitive to low concentrations of salt; and 5) interpenetration or compression of adsorbed polymers between two particles with high surface coverage leads to entropic repulsion or steric hindrance. A number of mathematical models have been presented to quantify entropic repulsion. Those of Mackor-vander Waals, Clayfield-Lumb, and Meir, are discussed by Lyklema (39).

Stability due to a hydration layer most likely accounts for very little stability over that due to the electrical double layer. The hydration layer would extend only a few water-molecule diameters from the surface of the particle. Thus, its effect would be observed for only very small distances, much less than the distance where the fate of the colloid is decided due to the interaction of the electrical double layer and London-van der Waals attraction. However, its effect should not be entirely neglected, as it is important in the short range interaction of particles and may influence the surface characteristics of the colloid.

## Coagulants

The chemicals commonly used fo- coagulation and flocculation of water and wastewater are the trivalent metals aluminum and iron (III), divalent metals calcium and iron (II), organic polyelectrolytes of the anionic, cationic and nonionic types, and activated silica. Aluminum sulfate, commonly called alum or filter alum, is the usual source of aluminum. There are probably three types of action which cause the removal of negatively charged collids when aluminum sulfate is added to a water or wastewater. These are discussed as follows:

1. First the trivalent aluminum cation neutralizes a portion of the negatively charged collids. Since $Al^{3+}$ exists primarily as a hydrated species (e.g. $Al(H_2O)_6{}^{3+}$), it is most likely that the free $Al^{3+}$ ion plays a small role at pH values of practical interest.
2. These hydrated aluminum ions behave as acids in the Bronsted sense and upon reaction with the alkalinity, or simply giving up $H^+$ ions to water, form a wide variety of monomeric species as follows: $[Al(H_2O_5(OH)]^{2+}$, $[Al(H_2O_4(OH)_3]^+$, $[Al(H_2O)_3(OH)_3]$, and $[Al(H_2O_2(OH)_4]^-$, and a wide variety of polymeric species formed when two or more

aluminum ions are bound together, probably by hydroxo bridges. All these positively charged species have a capacity to neutralize negatively charged colloids.

3. Finally, these tiny particles formed in the above two steps tend to be neutralized as the positive and negative particles come into contact, as the neutral species $Al(H_2O)_3(OH)_3$ is formed, and as the negatively charged sulfate, $SO_4^{2-}$, ion combines with any residual positively charged aluminum species. Upon approaching a neutral state and under slow mixing conditions, these particles come together and grow in size sufficiently large to settle under the influence of gravity. As the particles are coming together and growing in size or settling, additional colloidal particles may be removed by surface adsorption or enmeshment.

Iron (III) is usually added in the form of ferric chloride or ferric sulfate. It exists in aqueous solutions in the hydrated forms and removes negatively charged colloidal particles by mechanisms similar to those outlined above for aluminum.

Iron (II) usually obtained from ferrous sulfate, oxidizes rapidly at pH values used for coagulation to form iron (III).

The polyelectrolytes are thought to form bridges in the LaMer sense (35) and in the case of cationic polyelectrolytes reduced electrostatic repulsion of the negatively charged colloids occurs.

Calcium and activated silica are discussed in detail in the following chapters.

## III. ACTIVATED SILICA

### Introduction

Activated silica is a polymeric form of silica formed by partially "neutralizing" sodium silicate solutions. In water treatment practices, activated silica has a relatively long history of use. It was first found by Baylis (4) to be useful as a coagulant aid used in conjunction with alum and independently by Graf and Schworm (20) more than thirty years ago.

Some of the advantages reported in the literature (8, 33) are: 1) more effective coagulation, especially during cold weather, 2) larger more dense floc formation, 3) increased floc strength, 4) increased rates of coagulation, 5) savings in the primary coagulant alum, 6) broadening the effective pH range of alum, 7) longer filter runs, 8) increased color reduction, 9) higher quality finished water, and 10) increased capacity from existing plants. In addition, activated silica has been used in lime softening plants (8, 9, 51) to replace all or a portion of the alum used to remove fine calcium carbonate precipitates, resulting in significantly higher quality effluents.

A few cases have been reported in which activated silica has been used for clarification of industrial wastewaters. In one of these cases, activated silica was reported to aid in clarification of oily wastewater in a batch type treatment process. (43). A number of paper mills have reported that activated silica when used with alum provides an effective means of treating paper processed wastewaters (11, 34, 42).

There were only three papers found in the literature which indicated the use of activated silica to treat domestic sewage. These reported the results of laboratory and plant verification studies conducted in about 1940. Swope (67) found activated silica used with alum to be the best treatment based on economics and effectiveness of removal. The other chemicals tested were ferric chloride used both with and without lime, which proved as effective but more costly; and alum used alone, which proved slightly more economical but much less effective. Hurwitz and Williamson (29) found in a study--comparing the results using copperas, alum, or ferric chloride with and without activated silica, and copperas and lime--that activated silica used with copperas gave strikingly effective results at comparatively low cost. The third reported by Christenson and Lavine (13), indicated that a 40 per cent reduction of alum was possible when using ten parts per million activated silica, and that floc formation was much heavier and settled much faster than when using alum alone.

## Aqueous Silica

In nature silicon is not found free, but rather occurs as the oxy-compounds silica or silicate. Most rocks and minerals are silicates. Table III-1 illustrates the abundance of silicon containing minerals.

Due to the abundance of silica in nature, natural water is in almost constant contact with siliceous materials. It is therefore reasonable to expect essentially all natural waters to contain silica. Polzer (50) has summarized solubility data for water in equilibrium with various siliceous materials as follows: with quartz, 6 to 12 mg/l $SiO_2$; with amorphous silica, 100 to 140 mg/l $SiO_2$; and with clay materials, feldspars, micas, and other silicious rock-forming minerals, intermediate silica concentrations. He indicates it is the mineral type in contact with water which is the most important in determining the silica content of natural waters. In waters with pH values less than 9, the probable form of aqueous silica is monomeric silicic acid ($H_4SiO_4$) which protolyses above pH 9 to form various silicate ions. This ionization at higher pH values results in a higher total solubility

## TABLE III-1

## ABUNDANT SILICON-CONTAINING MINERALS*

| Mineral Group | Percentage of Minerals in Earth's Crust | Representative Formula and Common Name |
|---|---|---|
| Feldspars | 49 | $KAlSi_3O_8$, Orthoclase<br>$NaAlSi_3O_8$, Albite<br>$CaAl_2Si_2O_8$, Anorthite<br>$Na_4Al_3Si_3O_{12}Cl$, Sodalite |
| Quartz | 21 | $SiO_2$, Silica |
| Amphiboles | 15 | $CaSiO_3$, Wollastonite<br>$NaAlSi_2O_6$, Jadeite<br>$Ca_2Mg_5Si_8O_{22}(OH)_2$, Tremolite |
| Mica | 8 | $KAl_2Si_3AlO_{10}(OH)_2$, Muscovite<br>$K_2Li_3Al_4Si_7O_{21}(F,OH)_3$, Lepidolite |
| Non-Silicon | 7 | Carbonates, Sulfates, Sulfides Oxides, Some Minor Silicates and all others |

*Source: Reference 32.

of silica. This is demonstrated by data taken from Okuma, Goto, and Murai (45), shown in Figure III-1 for various temperatures. A recent summary (66) of silica equilibria data is shown in Table III-2 and illustrated in Figure III-2.

TABLE III-2

SILICA EQUILIBRIA

| Equilibrium Relationship | Log of Equilibrium Constant |
|---|---|
| $SiO_2(S)$ (amorphous) $+ 2H_2O = Si(OH)_4$ | - 2.7 |
| $Si(OH)_4 = SiO(OH_3)^- + H^+$ | - 9.46 |
| $SiO(OH)_3^- = SiO_2(OH)_2^{2-} + H^+$ | - 12.56 |
| $4Si(OH)_4 = Si_4O_6(OH)_6^{2-} + 2H^+ + 4H_2O$ | - 12.57 |

*Source: Reference 66.

## Preparation Techniques

One of the first methods of preparing activated silica for use as a coagulant aid was presented by Baylis (4) in 1937. Sodium silicate solution (41° to 42° Baumé) was diluted to 1.5% $SiO_2$ and treated with sulfuric acid. The acid, in a 20 to 40% $H_2SO_4$ dilution, was added to the sodium silicate solution while stirring until the alkalinity was reduced to 1100 to 1300 mg/l as calcium carbonate.

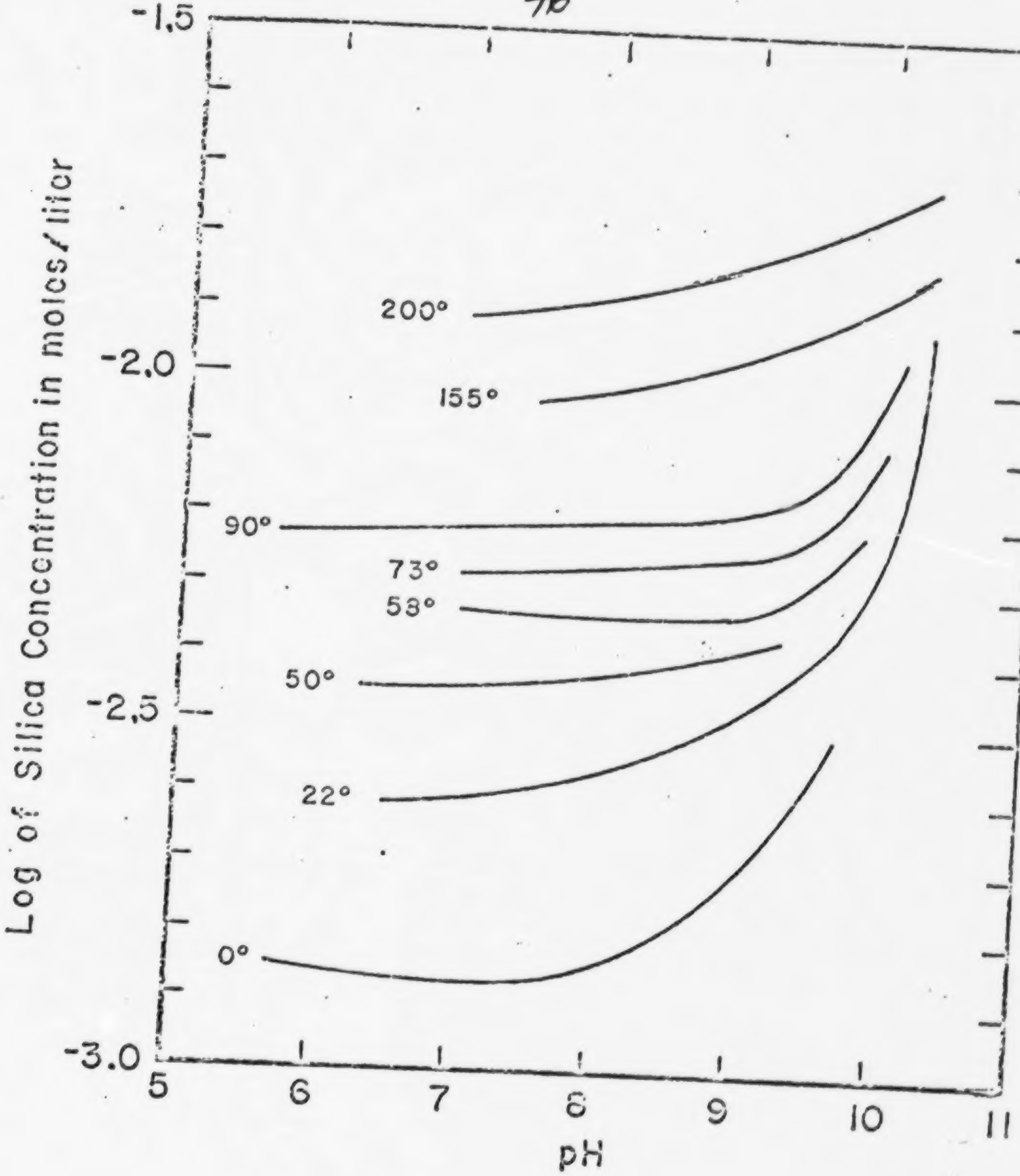

FIGURE III-1. TOTAL SOLUBILITY OF SILICA AS A FUNCTION OF pH AND TEMPERATURE.

Temperatures given in degrees Centigrade.
Source: Reference 45.

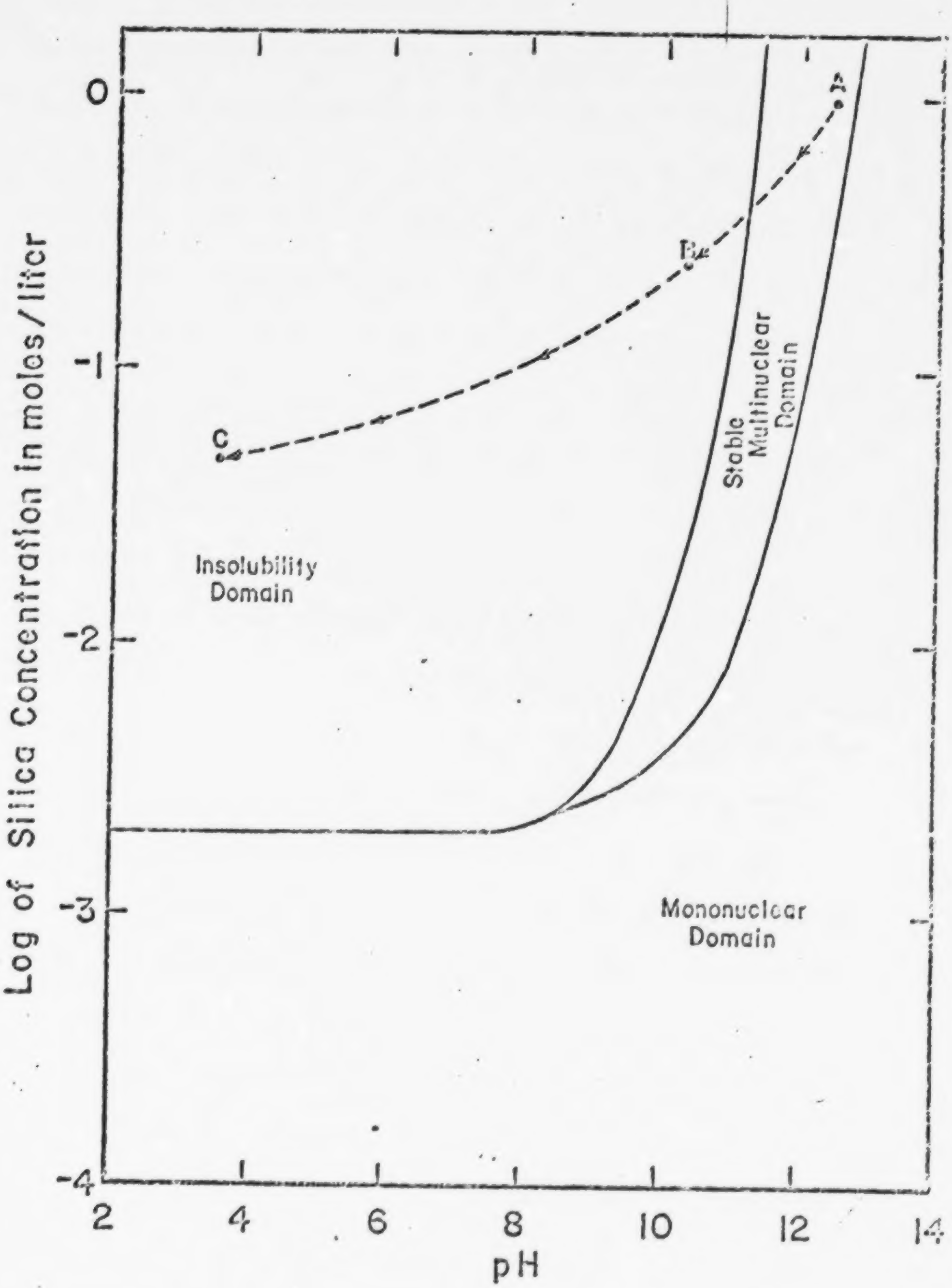

FIGURE III-2. SPECIES IN EQUILIBRIUM WITH AMORPHOUS SILICA.

Points A, B, and C, are referred to in a later section of the text. Source: Reference 66.

This mixture was allowed to stand one or two hours then further diluted to approximately 0.6% $SiO_2$, then was used in this form. The other method developed by Graf and Schworm (20) involved the addition of 1% alum solution to a 1% silicate solution in the ratio 4 to 1. This mixture was then used immediately as a coagulant aid with alum.

Since Baylis and Graf and Schworm first introduced their procedures, a wide variety of reagents have been used to activate or treat sodium silicate solutions for this purpose. Some of the more common activating agents (all acids) which have been used successfully are the strong mineral acids, sulfuric and hydrochloric; the acidic salts, sodium bicarbonate, aluminum sulfate, and ammonium sulfate; and the gases, chlorine and carbon dioxide. In addition sodium silicate solutions have been activated by passing them through cation exchange resins of the hydrogen form. Sodium silicate is commercially available in powder and solution forms with $SiO_2/Na_2O$ ratios of 0.5 to 4.0. Reagent grades of sodium metasilicate ($Na_2SiO_3$) are frequently used to prepare stock solutions for laboratory use.

In the studies reported herein the preparation technique was as follows:

1. Reagent sodium metasilicate was used to

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In the studies reported herein the preparation technique was as follows:

1. Reagent sodium metasilicate was used to

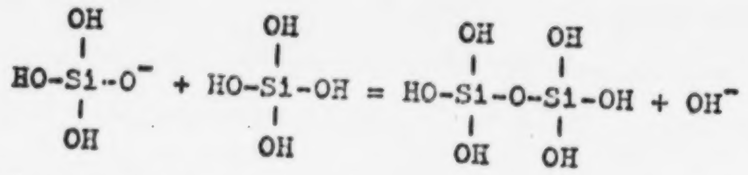
prepare a 1.0-molar stock solution (i.e. 6.0% $SiO_2$).

2. Sufficient 0.5 molar sulfuric acid and distilled water were added to the stock solution to yield a pH of approximately 10.3 and a molarity of 0.25 (i.e. 1.5% $SiO_2$). This pH was selected since lower pH values caused gel formation so quickly that dilution was impossible and at higher pH values the polymerization was too slow to be practical.
3. The extent of polymerization was followed in a Hach Turbidimeter Model 2100 to an appropriate turbidity, usually 100 Jackson Turbidity Units (JTU) unless otherwise specified.
4. Upon reaching the desired turbidity this polymerized 0.25 molar solution was diluted to a final concentration of 0.05 molar (i.e. 0.3% $SiO_2$) and the pH reduced to 3.0 to 4.0 with sulfuric acid. This solution was stored and used for no more than one week.

This procedure proved to be a convenient laboratory technique for preparing the activated silica solutions. After a couple trials, for given stock solutions of sodium silicate and sulfuric acid, the exact quantities could be added and the desired pH range achieved. Turbidity was considered to be indicative of polymer size. Thus, by observing the turbidity during the polymerization or aging phase and diluting at the appropriate time, relatively consistent polymer sizes could be achieved from batch to batch. Other means of characterizing the polymer were considered. Aging time, the method used frequently for plant operations, was considered to be less desirable since it was found that minor differences in pH after addition of acid produce significantly different times to reach a specific turbidity. Spectroscopic studies in the ultraviolet (190 to 390 mμ), visible (350 to 750 mμ), and infrared (2 to 15 μ) regions showed little promise of characterizing the polymer. A relatively broad absorption peak was found in the infrared region at approximately 9.3 microns for the polymeric form of silica, but not for the monomeric form. This is the region where absorption due to Si-O-Si vibration is known to occur (73), therefore this may prove to be useful in characterizing the polymer. Several difficulties encountered in the preliminary infrared studies are as follows: 1) sodium chloride, the usual window material, cannot be used due to its solubility in aqueous solutions; 2) water has very high absorption in the infrared region, necessitating the need for very thin layers (absorption through 0.025 mm layers of water, using the thinnest spacer available, produces only about thirty per cent transmittance in the 8 to 10 micron region; using no spacers, capillary layers of water produce transmittances of approximately 60 per cent); 3) absorption peaks in the 8 to 10 micron region using capillary layers were indistinguishable for activated silica sols aged to various turbidities in the range of 50 to 175 JTU; and 4) calcium flouride windows, used to replace the soluble sodium chloride windows, were found difficult to clean as polymeric silica appeared to be adsorbed by the surface of the windows. Viscosity measurements were also considered to characterize the polymers. However due to the ease and apparent success of the turbidity method these were not pursued in depth.

## Polymer Formation and Physical Characteristics

As early as 1938 Hurd (28) in a review of theories of mechanisms of gel formation of silicic acids, concluded that condensation of silicic acid to form polysilicic acid structures was the mechanism by which silicic acids gels were formed. Much later in 1955, Greenberg and Sinclair (21) discussed a mechanism of polymerization which proceeds by reaction of singularly ionized silicic acid with un-ionized silicic acid and polysilicic acid as follows:



$$\mathrm{HO{-}\overset{OH}{\underset{OH}{Si}}{-}O^{-}} + \mathrm{HO{-}\overset{OH}{\underset{OH}{Si}}{-}OH} = \mathrm{HO{-}\overset{OH}{\underset{OH}{Si}}{-}O{-}\overset{OH}{\underset{OH}{Si}}{-}OH} + \mathrm{OH^{-}} \qquad \text{(III-1)}$$

Lange and Spencer (37) recently discussed both mechanisms and concluded that both contributed to the polymerization process to some extent. Condensation, the first of these reactions may be shown in terms of the functional groups as follows:

$$2\ \mathrm{SiOH} = \mathrm{SiOSi} + \mathrm{H_2O} \qquad \text{(III-2)}$$

and is believed to dominate under acidic conditions where equilibrium conditions favor the existence of the un-ionized species. The other reaction involves the production of hydroxyl ions and is shown in terms of the functional groups as follows:

$$\mathrm{SiOH} + \mathrm{SiO^{-}} = \mathrm{SiOSi} + \mathrm{OH^{-}} \qquad \text{(III-3)}$$

and predominates under basic conditions where ionized species dominate.

Bechtold (5) in light scattering and freezing point depression studies found an apparent functionality of slightly over two (2.0004 to 2.05) which indicates the formation of linear polymers since only two of the four functional groups of each silicon atom react. He believed the functionality was not exactly two but slightly greater, indicating occasional reaction of the third and fourth functional groups, resulting in some cross connections.

Audsley and Aveston (3) likewise arrived at this conclusion, indicating the third and fourth hydroxyl groups are much less reactive, thus a functionality of very nearly, but slightly greater than two. However, they found viscosity measurements were inconsistent with the idea of polysilicic acid molecules existing as extended chains, thus chains must be sufficiently contracted or the small amount of branching is sufficient to treat them as spheres.

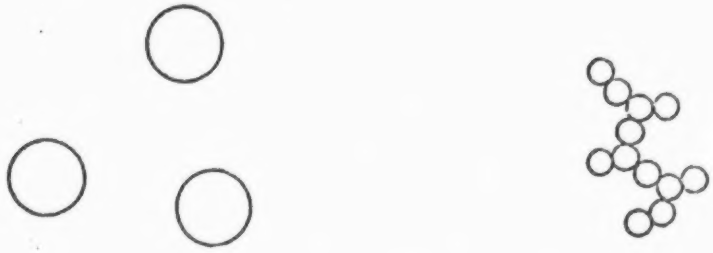
Okura, Goto, and Murai (45) presented an interesting view of two types of colloidal particles formed during silica gel formation. When polymerization proceeds under basic conditions---well above the isoelectric point of pH 2 to 3---electrical double layer repulsion is sufficient to prevent particles from colliding, therefore discrete particles are formed. On the other hand, when polymerization proceeds under neutral or acidic conditions--closer to the isoelectric point where the electrical double layer repulsion is lower--particles are formed, then collide to form larger aggregates of particles. The particles formed under these two conditions are illustrated in Table III-3.

A number of investigators (3, 5, 17) have found the molecular weights vary upward to about $10^6$ just prior to gel formation.

The preparation technique outlined in the preceding section is illustrated in Figure III-2 to demonstrate the effect of dilution and acidification on the solubility of silica. Point A is the pH and concentration of the one molar stock solution of sodium metasilicate. Upon acidification and dilution, point B is arrived at where the silica is in a state of supersaturation with respect to solubility, thus polymerization occurs. Further dilution and pH reduction brings the activated silica solution to Point C, where it is stored ready for use.

TABLE III-3

SCHEMATIC REPRESENTATION
TWO TYPES OF COLLOIDAL SILICA PARTICLES*



Particles Formed in Basic Solutions**

Particles Formed in Neutral or Acidic Solutions

* Source: Reference (45)
** The conditions used to prepare activated silica for the studies reported herein.

Figure III-3, taken from Merril and Spencer (41), demonstrates the rate of polymerization as a function of

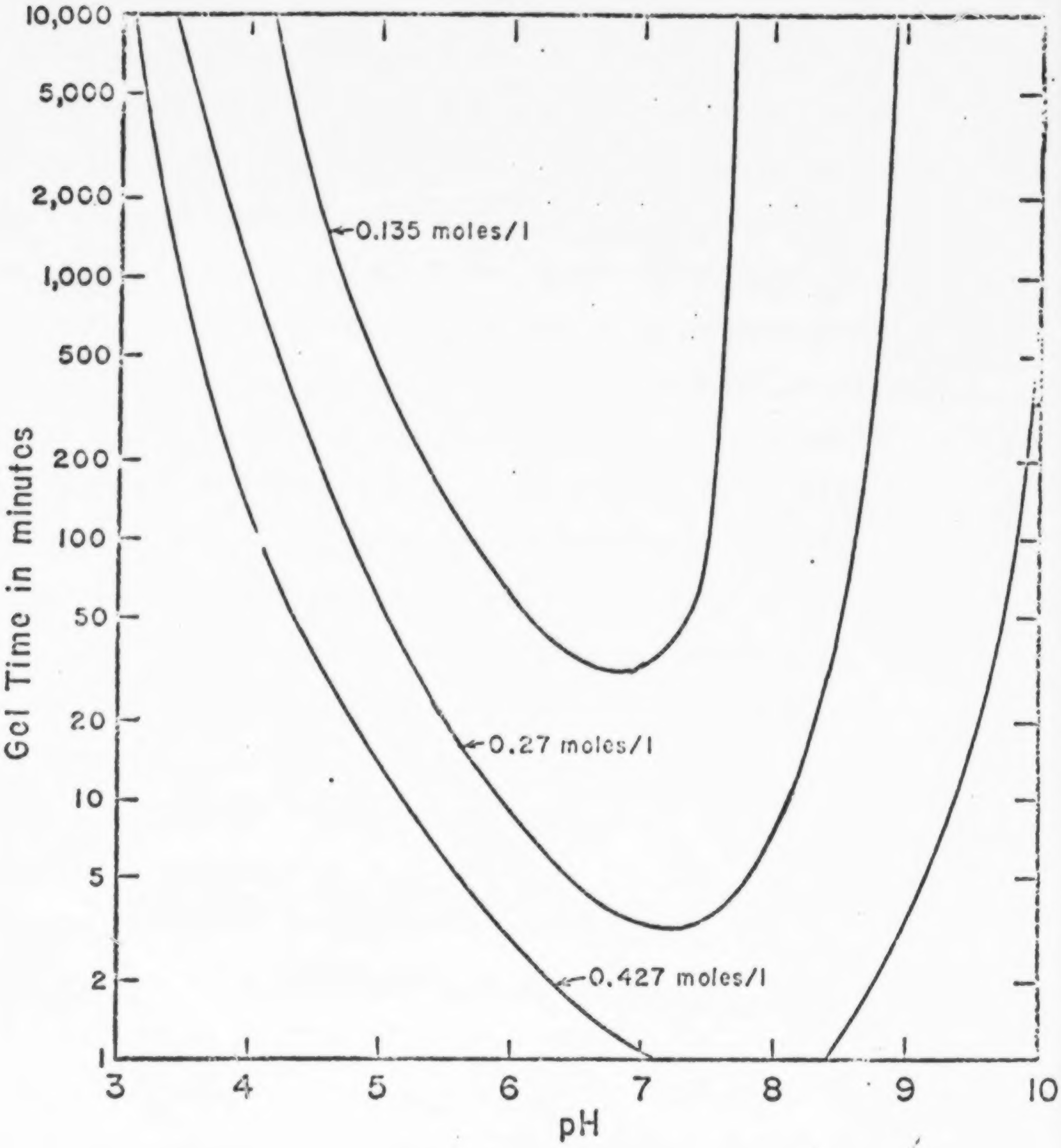


FIGURE III-3. VARIATION OF GEL TIME AS A FUNCTION OF pH AND SILICA CONCENTRATION.

Source: Reference 41.

pH using time required to form gel as a parameter of polymerization rate. These data are for sodium silicate solutions having $SiO_2/Na_2O$ ratios of 3.3 and using sulfuric acid for pH adjustment. It should be noted that at both high and low pH values, gel times approach infinity, thus the stability of the stock sodium metasilicate solution at high pH (i.e. point A in Figure III-2) and the relatively stable 0.05 molar activated silica solution at low pH (i.e. point C in Figure III-2). The relative stability of an activated silica solution prepared as described above is demonstrated in Figure III-4 where turbidity of a sample was followed over a period of time. Since all studies were conducted with samples stored for no more than one week it is apparent that there is little change in the polymer size during this period. Gel formation occurs at a turbidity of approximately 250 JTU.

The results of a coagulation study using lime and various types of activated silica to compare the effect of aging time or polymer size are shown in Figure III-5. The effectiveness of the activated silica appears to be relatively independent of polymer size except the smaller polymers seem to be slightly more effective. In fact, the multinuclear species prepared by diluting one molar stock solution (designated by point A in Figure III-2) to 0.05 molar without pH adjustment and used immediately,

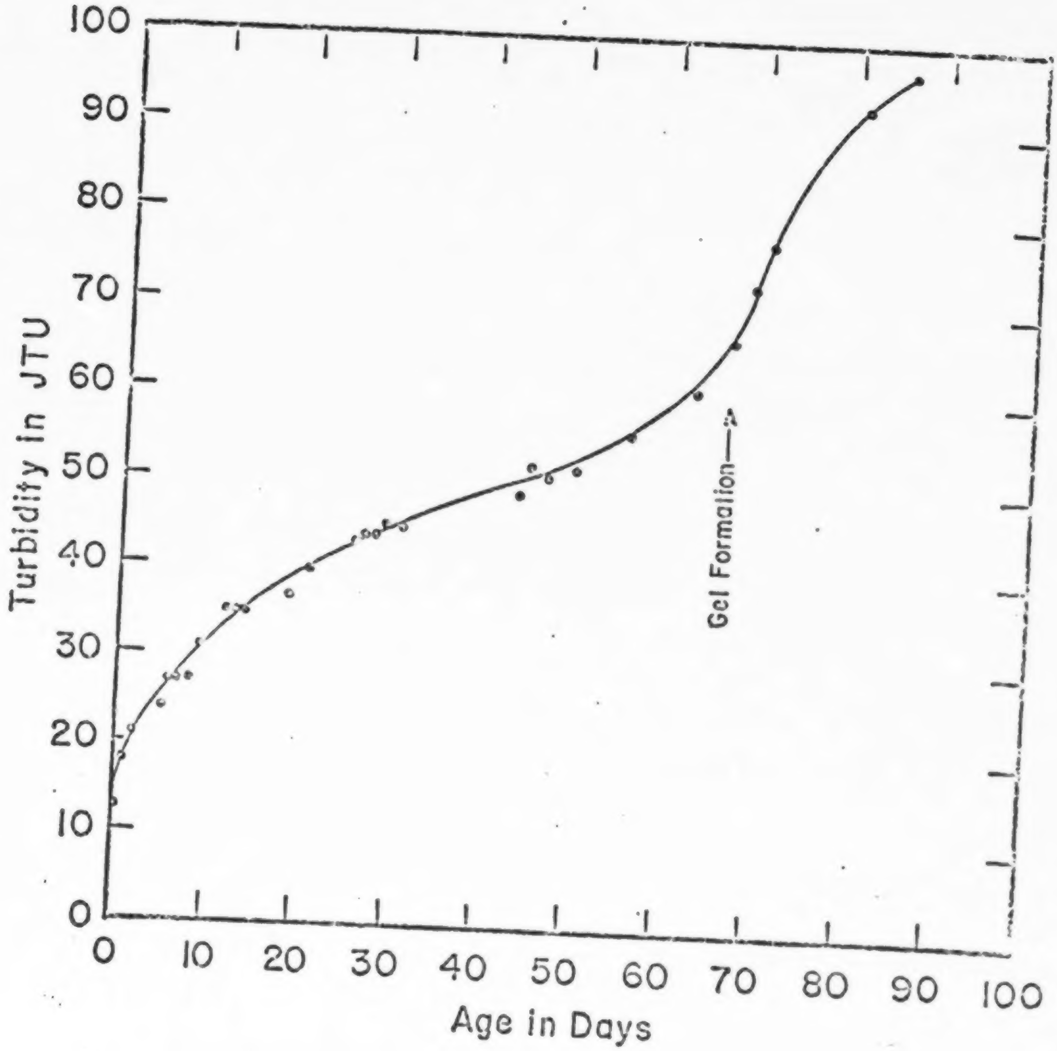


FIGURE III-4. POLYMERIZATION DURING STORAGE OF 0.05 MOLAR ACTIVATED SILICA AS INDICATED BY INCREASING TURBIDITY.

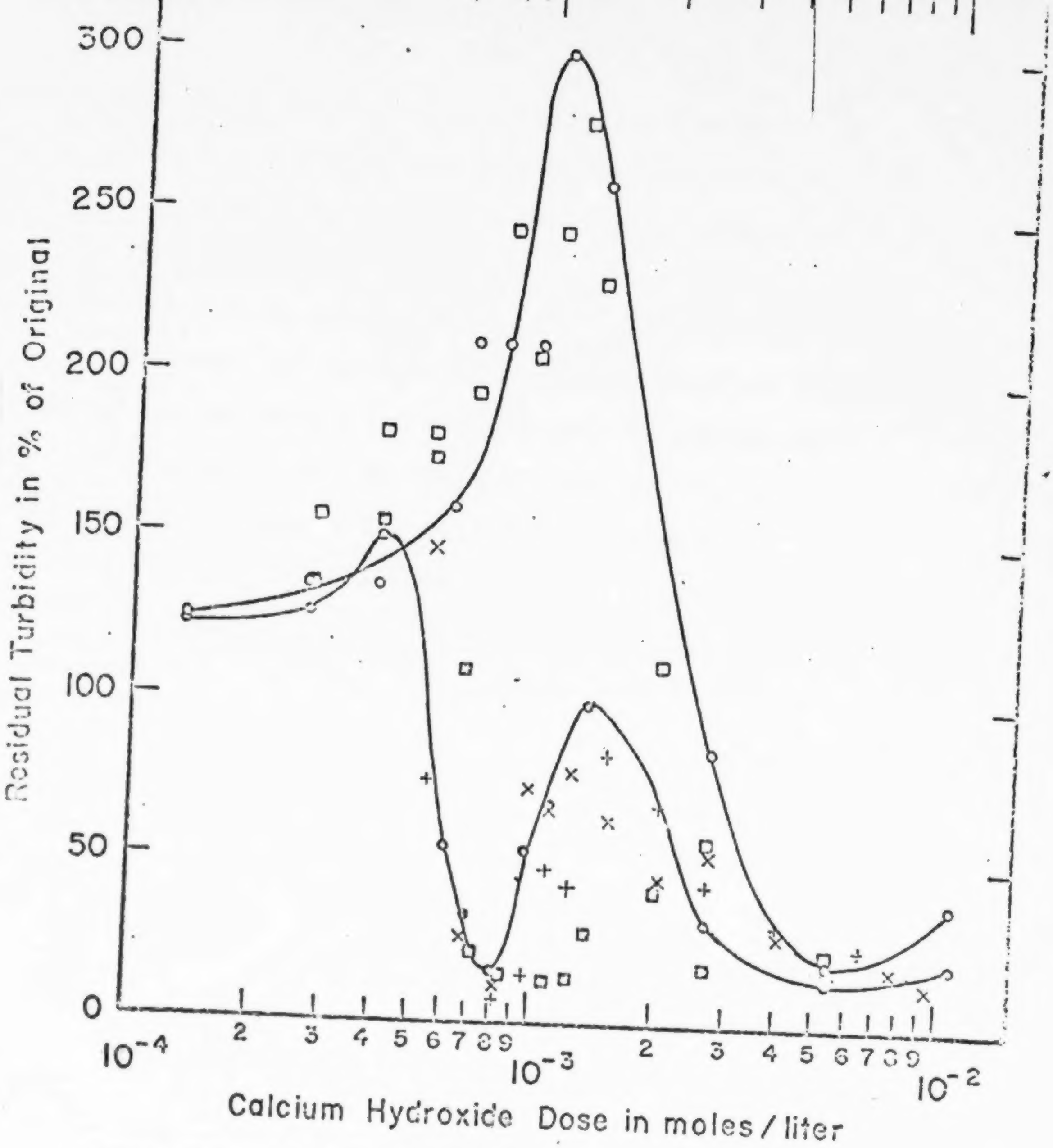


FIGURE III-5. EFFECT OF ACTIVATED SILICA POLYMER SIZE ON CLARIFICATION OF A SUSPENSION OF 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE USING CALCIUM HYDROXIDE.

The various activated silica types are: no activated silica represented by open circles; monomeric silica represented by open squares; multi-nuclear silica represented by solid squares; activated silica aged to 50 JTU represented by crosses; activated silica aged to 100 JTU represented by solid circles; activated silica aged to 200 JTU represented by + symbols. All activated silica additions were made at 6.0 mg/l as $SiO_2$.

appear to be more beneficial than those aged to form larger polymers. However, the monomeric form prepared by dissolving sodium metasilicate crystals in distilled water to form an 0.05-molar solution was ineffective, residual turbidities being almost identical to the systems using lime alone. It appears that aging time makes little difference except that gel formation must be prevented since handling difficulties would be encountered, and it has not been demonstrated that solutions which had once formed gel would be effective. Packham (49) also found the degree of aging to be of little consequence.

# IV. AQUEOUS CALCIUM

## Introduction

Calcium is widely distributed and the fifth most abundant element in the earth's crust. Limestone, a common rock, is an impure calcium carbonate. Dolomite, a magnesium containing limestone is $CaCO_3 \cdot MgCO_3$. Other natural forms of calcium carbonate include calcite, aragonite, chalk, marble, marine shells, and pearls. Although these are all chemically composed chiefly of $CaCO_3$, their different modes of formation have caused them to be quite different in general properties, appearance, and usefulness. Calcium is also relatively abundant in nature combined with sulfate as anhydrite and gypsum, with fluoride as fluorite and fluorspar, and with phosphate as a wide variety of apatites frequently formulated as: $Ca_{10}(PO_4)_6(OH,Cl,F)_2$. Solubilities of some of these naturally occurring calcium compounds, given in terms of grams of compound per 100 cc of water at about 25°C, are as follows: calcite, 0.0014; aragonite, 0.00153; anhydrite, 0.209; gypsum, 0.241; and fluorite, 0.0017 (73).

Due to the abundance of calcium containing materials in nature and their relatively high solubility, virtually all natural waters contain significant concentrations of calcium. In reporting water supply characteristics, calcium is frequently included with and reported only in terms of hardness. Hardness is a measure of the polyvalent cations, however most other polyvalent cations are present in insignificant concentrations compared to calcium and magnesium. Of these two, calcium frequently accounts for the major portion of the hardness. Soft waters, those waters containing less than about 75 mg/l hardness expressed as $CaCO_3$, are found in the northwestern, northeastern and some southern sectors of the United States. Hard waters, containing more than 150 mg/l and frequently as much as 300 mg/l, are found in most of the central states. Virtually all parts of the United States, therefore have water supply containing significant concentrations of calcium. The detrimental effects due to the presence of calcium in water supplies are associated chiefly with those of hardness. The most significant being the increase of soap consumption and related laundry problems; scale formation in hot-water pipes, heaters and boilers; and in certain industrial uses.

Millions of tons of limestone are mined each year, then ground or crushed and heated to about 900°C to produce quicklime as follows:

$$\underset{\text{(limestone)}}{CaCO_3} = \underset{\text{(quicklime)}}{CaO} + CO_2 \qquad \text{(IV-1)}$$

Hydrated lime is produced upon addition of water to quicklime as follows:

$$\underset{\text{(quicklime)}}{CaO} + H_2O = \underset{\text{(hydrated lime)}}{Ca(OH)_2} + \underset{\text{(15,600 cal./mole)}}{\text{heat}} \qquad \text{(IV-1)}$$

Large quantities of lime are used for treatment of waters and wastewaters. Quicklime, available in various sizes up to 8-inch lumps, may be pulverized and fed dry to the water being treated where hydration occurs rapidly due to its affinity for water. More frequently, particularly in lime softening plants, it is first slaked using mechanical equipment where it is mixed with water and held for approximately 30 minutes depending on the lump size. The slaked or hydrated lime is then fed to the water being treated in a slurry of 10 to 15% concentration. When hydrated lime is used, it is generally fed dry and frequently used when smaller quantities are required such as for small softening plants and acid waste neutralization.

## Solubility and Equilibrium Data

Equilibrium and ionization relationships are shown in Table IV-1.

Figure IV-1 has been prepared using the data shown on Table IV-1 and according to procedures presented by Weber and Stumm (75). Since this illustration is intended

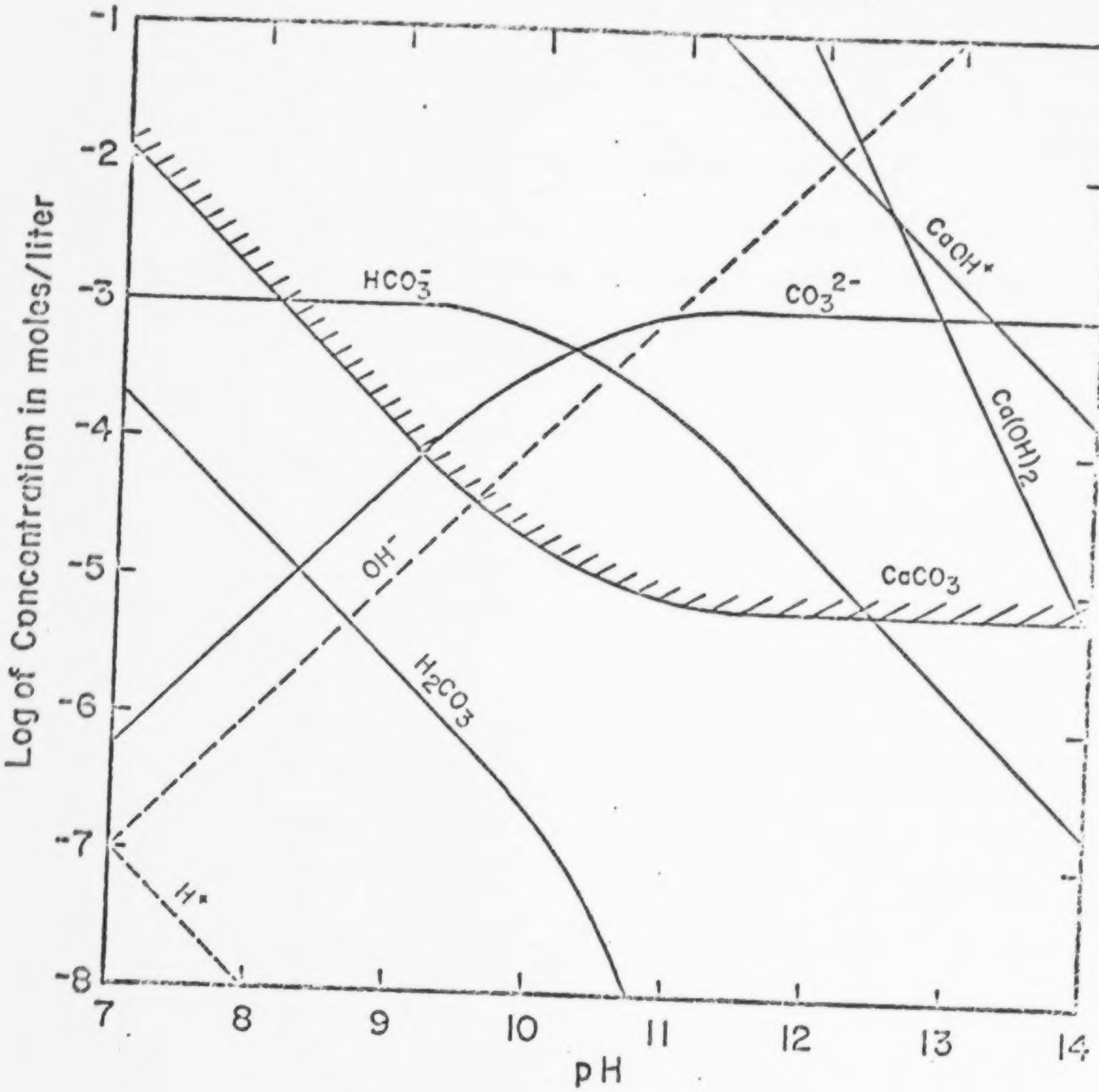


FIGURE IV-1. SOLUBILITY EQUILIBRIA OF CALCIUM IN A $10^{-3}$ MOLAR CARBONATE SYSTEM.

only to show the effect of pH on solubility of calcium carbonate, correction for ionic strength has not been included. Figures IV-2 and IV-3, likewise show solubility of calcium in $10^{-3}$ and $10^{-5}$ molar phosphate systems, respectively.

TABLE IV-1

IONIZATION AND EQUILIBRIUM RELATIONSHIPS

| Equilibrium Relationship | Log of Equilibrium or Ionization Constant* |
|---|---|
| $Ca(OH)_2(s) = Ca^{2+} + 2(OH^-)$ | - 5.26 |
| $Ca(OH)_2(s) = CaOH^+ + OH^-$ | - 3.75 |
| $CaCO_3(s, calcite) = Ca^{2+} + CO_3^{2-}$ | - 8.18 |
| $Ca_{10}(PO_4)_6(OH)_2 = 10Ca^{2+} + 6(PO_4^{3-}) + 2(OH^-)$ | -90 |
| $H_2CO_3 = H^+ + HCO_3^-$ | - 6.35 |
| $HCO_3^- = H^+ + CO_3^{2-}$ | -10.25 |
| $H_3PO_4 = H^+ + H_2PO_4^-$ | - 2.23 |
| $H_2PO_4^- = H^+ + HPO_4^{2-}$ | - 7.21 |
| $HPO_4^{2-} = H^+ + PO_4^{3-}$ | -12.32 |
| $H_2O = H^+ + OH^-$ | -14.0 |

* Source of Constants, Reference (10) except Reference (19) used for hydroxylapatite.

## Calcium Coagulation

Calcium when used as a coagulant undergoes precipitation

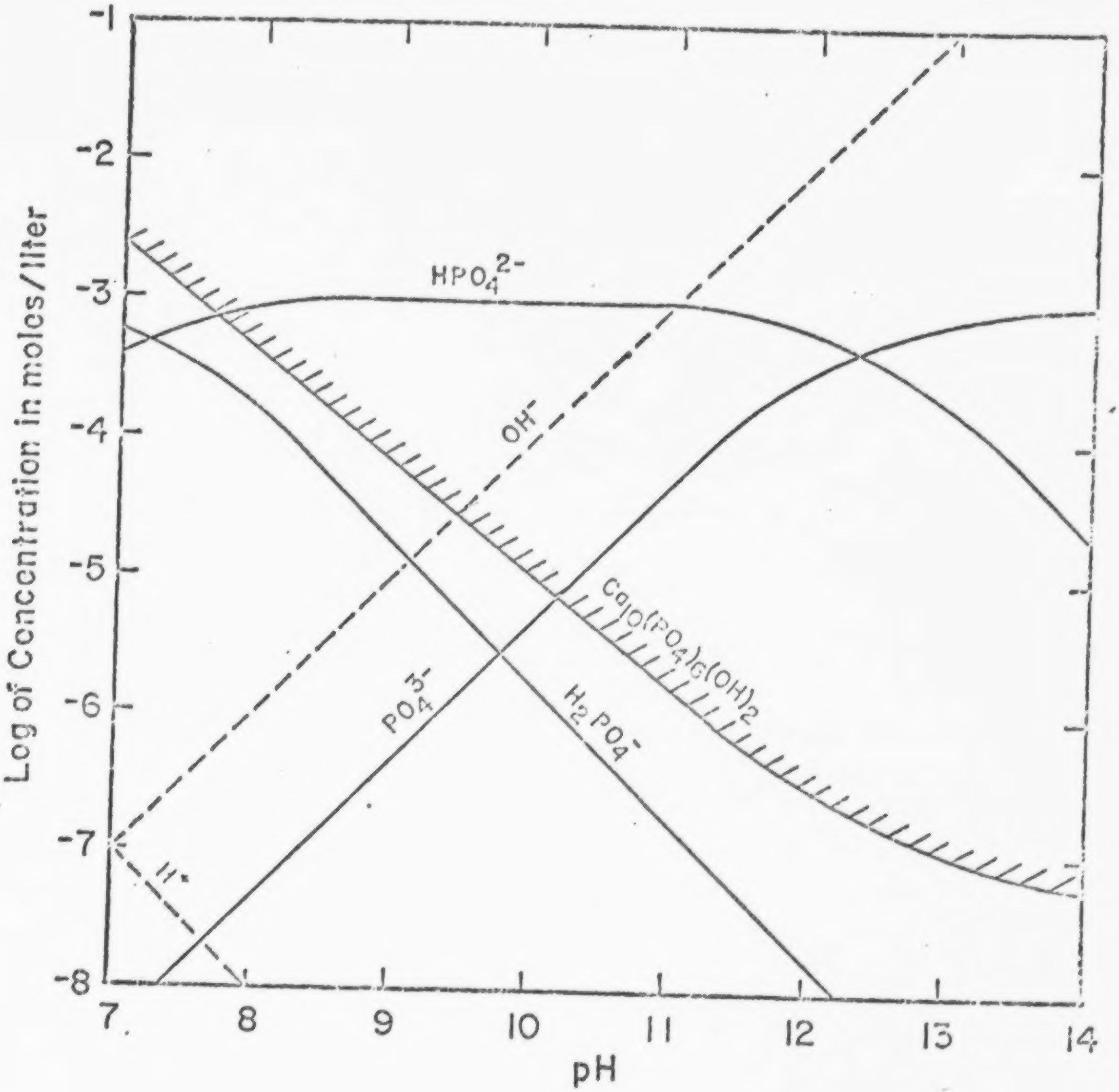


FIGURE IV-2. SOLUBILITY EQUILIBRIA OF CALCIUM IN A $10^{-3}$ MOLAR PHOSPHATE SYSTEM.

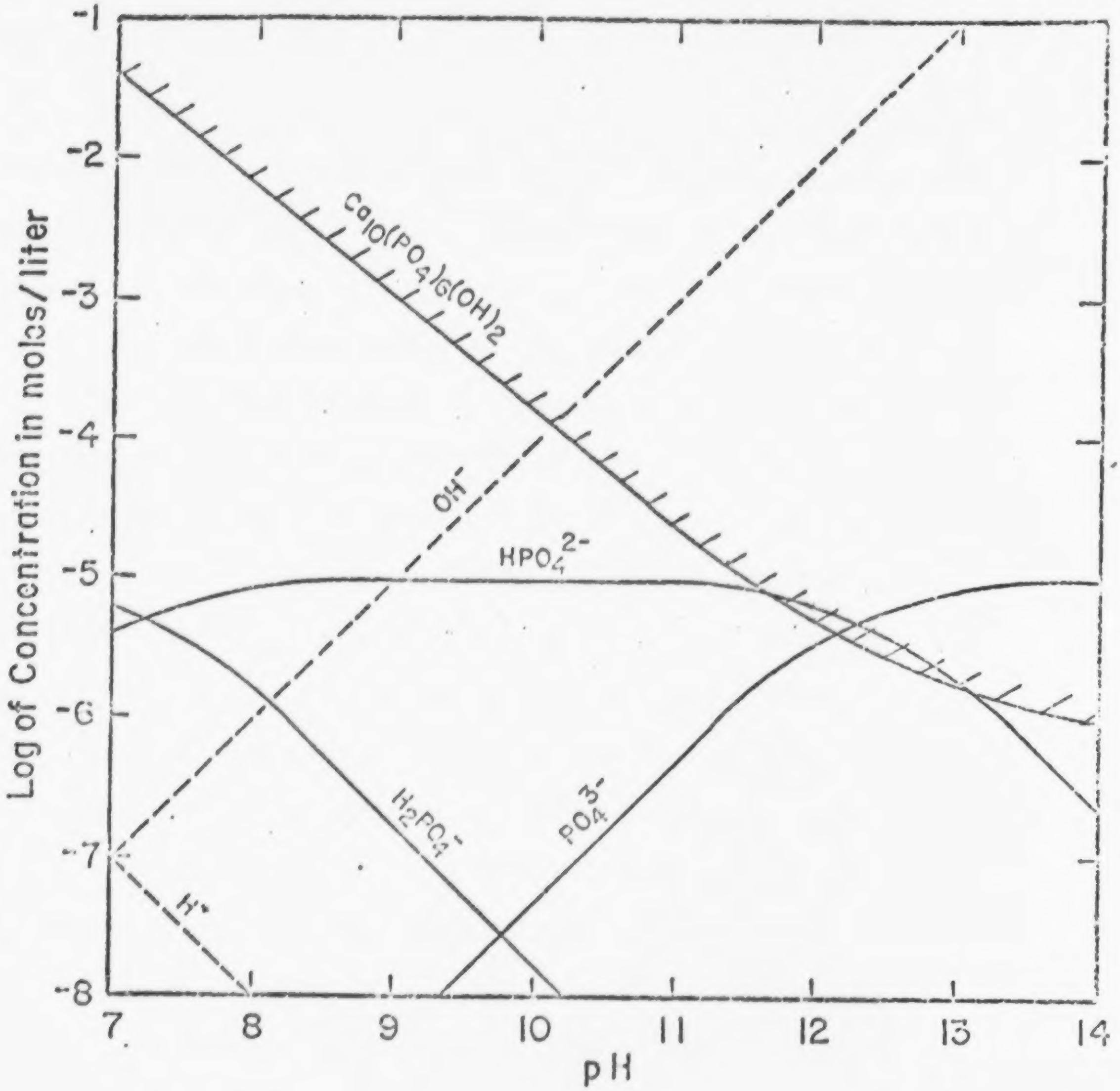


FIGURE IV-3. SOLUBILITY OF CALCIUM IN A $10^{-5}$ MOLAR PHOSPHATE SYSTEM.

reactions when introduced into natural waters or wastewaters as indicated in Table IV-1. It may also react to neutralize acids in addition to its primary purpose of compressing the electrical double layer of the colloids.

Upon addition of lime to natural waters or wastewaters dissolution occurs at a relatively slow rate since it can take place only at the surface of the particles. Diffusion of molecules away from the solid surface is also relatively slow so that the solution in the immediate vicinity of the solid approaches saturation concentration, thus reducing the concentration gradient and dissolution rate. To increase the rate of dissolution, particles size may be decreased to increase surface area and mixing may be provided to bring unsaturated solution in contact with the solid surface. The hydroxide from dissolution of $Ca(OH)_2$, once in solution, increases the pH almost instantaneously by neutralizing any acid present and if added in excess of the acid, remains in solution as free hydroxide ions, resulting in a relatively high pH solution.

Calcium ions will compress the electrical double layer of colloids present almost immediately after dissolution. However, they will tend to be removed relatively slowly by formation of calcium carbonate and calcium hydroxylapatite precipitates if carbonates and phosphates are present, thus reducing their effect on the electrical double layer. Calcium carbonate particles formed in this manner, tend to be small, dense, and primarily calcite and to some extent aragonite, a metastable form (23). Black and Christman (6) reported average electromobility values of about -1.0 $\mu$/sec/v/cm for $CaCO_3$ particles formed with the addition of varying dosages of lime in the pH range 9 to 11 to a synthetic water containing CaCl and $NaHCO_3$. The formation of these calcium carbonate particles occurs at a relatively slow rate. The rate is determined by the nucleation rate, which may be accelerated by the presence of seed crystals or other particles, and by the rate of crystal growth which occurs only at the surface of the forming particle.

According to X-ray defraction pattern analysis, five different calcium phosphates can be precipitated from aqueous solutions. These are: $Ca(H_2PO_4)_2$; $Ca(H_2PO_4) \cdot H_2O$; $CaHPO_4$; $CaHPO_4 \cdot 2H_2O$; and a crystal precipitate of variable composition called hydroxylapatite and having a base formula of $Ca_5(OH)(PO_4)$ (69). The only one of these five formed under concentration and pH conditions encountered in water and wastewater treatment is the hydroxylapatite, whose crystals are generally formed at a more rapid rate than those of the calcium carbonate (19). As equilibrium conditions are approached, and lime is added to excess of that precipitated as calcium carbonate or hydroxylapatite, the solution will contain $Ca^{2+}$, $CaOH^+$, $Ca(OH)_{2(ag)}$, $CaCO_3$, and hydroxylapatite. of the two ionic calcium species, $Ca^{2+}$ and $CaOH^+$, the $Ca^{2+}$ will dominate at lower pH values. For example even as high as pH 11 $CaOH^+$ is equal to only about 3.2% of $Ca^{2+}$. The calcium ions are considered not to be hydrated, although there will be preferential alignment of water molecules around the ion.

It is frequently necessary to reduce the pH after treating water with lime. This may be accomplished by the addition of mineral acids. When water is softened using lime it is frequently neutralized by the addition of carbon dioxide usually generated from combustion of natural gas.

# V. COAGULATION OF SYNTHETIC SYSTEMS

## Experimental Procedure

The experimental phase of this study was directed primarily at identification of types of wastewaters most susceptible to treatment using lime and activated silica and to determine which factors are significant in predicting the feasibility of lime-activated silica treatment for a particular water. To facilitate control of the various parameters, synthetic systems were used. These synthetic systems were made using distilled water with addition of known quantities of substances to produce the desired characteristics. Studies of natural waters and wastewaters, reported in the following chapter, were conducted primarily to confirm findings of synthetic systems.

Coagulation and flocculation results are evaluated by examining the characteristics of the clarified supernatant and/or of the solid floc portion. TeKippe and Ham (66) recently summarized techniques for evaluating the coagulation-flocculation process; these include the following: 1) conventional jar test, 2) modified jar test, 3) speed of floc formation, 4) visual floc size

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comparisons, 5) floc density, 6) settled floc volume, 7) floc volume concentration, 8) residual coagulant concentration, 9) silting index, 10) filtrability number, 11) membrane refiltration, 12) inverted gauze filtration, 13) cation exchange capacity, 14) surface area concentration, 15) conductivity, 16) zeta potential, 17) streaming potential, 18) colloid titration, 19) pilot column filtration, 20) filtration parameters, 21) cotton-plug filtration, and 22) electronic particle counting.

Most of these techniques have found only limited application. Many of the techniques have been developed for a specific plant where a measurement was found to correlate with effective treatment for a particular water and treatment scheme, but are not necessarily applicable to other waters. Still others have extensive use in both research and control of treatment plant operations. The three best known measurements or techniques are discussed below; these include: 1) zeta potential measurement, 2) membrane refiltration, and 3) the conventional jar test.

Zeta potential or electrophoretic mobility measurements, which are accomplished by microscopically measuring particle velocities in water after the addition of chemical coagulants, has frequently been used in coagulation research. Black and coworkers, for example, have done a number of studies in which electrophoretic measurements have been so employed. One such study examined the effect on the mobility of various clay suspensions of treatment with alum, starch, and a number of polyelectrolytes (7). Riddick (55) has pioneered the use of electrophoresis for water treatment plant coagulation control.

Membrane refiltration was first presented by Smellie and LaMer (62). The technique consists of filtering a suspension through a membrane filter under constant pressure to form a filter cake. The filtrate is then refiltered through the cake and membrane. The time required to filter a specific volume is the parameter used to compare treatment schemes. LaMer and Healy (36) provide an effective summary of this work. Slater and Kitchener (61) have discussed the validity of some aspects of the theoretical development when used to study the mechanism of flocculation by polymers.

The conventional jar test is by far the most widely used approach both in research and plant control. In this technique, samples are stirred with several different dosages of coagulant chemical, followed by quick mix to distribute the chemicals, a slow mix to allow for floc growth, and finally a period of settling. After settling, samples of supernatant are withdrawn for turbidity measurements and the degree of clarification taken as a measure of the effectiveness of treatment. Many of the other measurements listed above may be used on samples taken from the jar test, however turbidity is by far the most common.

The conventional jar test technique was used in the studies reported herein. A detail description of the procedure is included in the appendix. Some of the advantages of this approach include: 1) of the methods previously listed, this technique most nearly approaches prototype flow-through units, recognizing the scale and batch-reactor restrictions; 2) the results are based on clarification of the supernatant, which is the primary concern in wastewater treatment; 3) analyses other than turbidity may conveniently be made on the supernatant; and 4) it allows visual comparison of floc formation and settling conditions, which although difficult to quantify, allows additional insight into the system.

## Results and Discussions

The results of the studies with synthetic systems are presented in the following sections. These sections include discussion of: 1) low alkalinity systems, specifically $10^{-3}$ molar in sodium bicarbonate, where the benefit of activated silica used in conjunction with lime is demonstrated; 2) effects of alkalinity where the benefits of activated silica are observed in low but not high alkalinity systems; 3) pH effect where pH as such is demonstrated to have little effect relative to that of alkalinity; and 4) phosphate effect, which under certain conditions is shown to overshadow the effect of activated silica.

## Low Alkalinity Systems.

This phase of the study was directed at examining, in detail, the effect of type and concentration of colloids and the effect of varying activated silica concentration on the results noted in the preliminary data presented in Figure I-2. The first coagulation study was conducted using varying concentrations of lime in the form of $Ca(OH)_2$ and activated silica aged to a turbidity of 100 JTU before dilution. The test suspension was comprised of 150 mg/l bentonite dispersed in a $10^{-3}$ molar solution of sodium bicarbonate. As noted in the preliminary data presented in Figure I-2, significant reduction in the lime requirement for clarification is possible when activated silica is used. Data in Figure V-1 indicate residual turbidities after 10 minutes of settling as a function of lime and activated silica dosages. Residual turbidity contours are included to outline the zones of effective clarification. It can be noted that lime requirements for reducing the

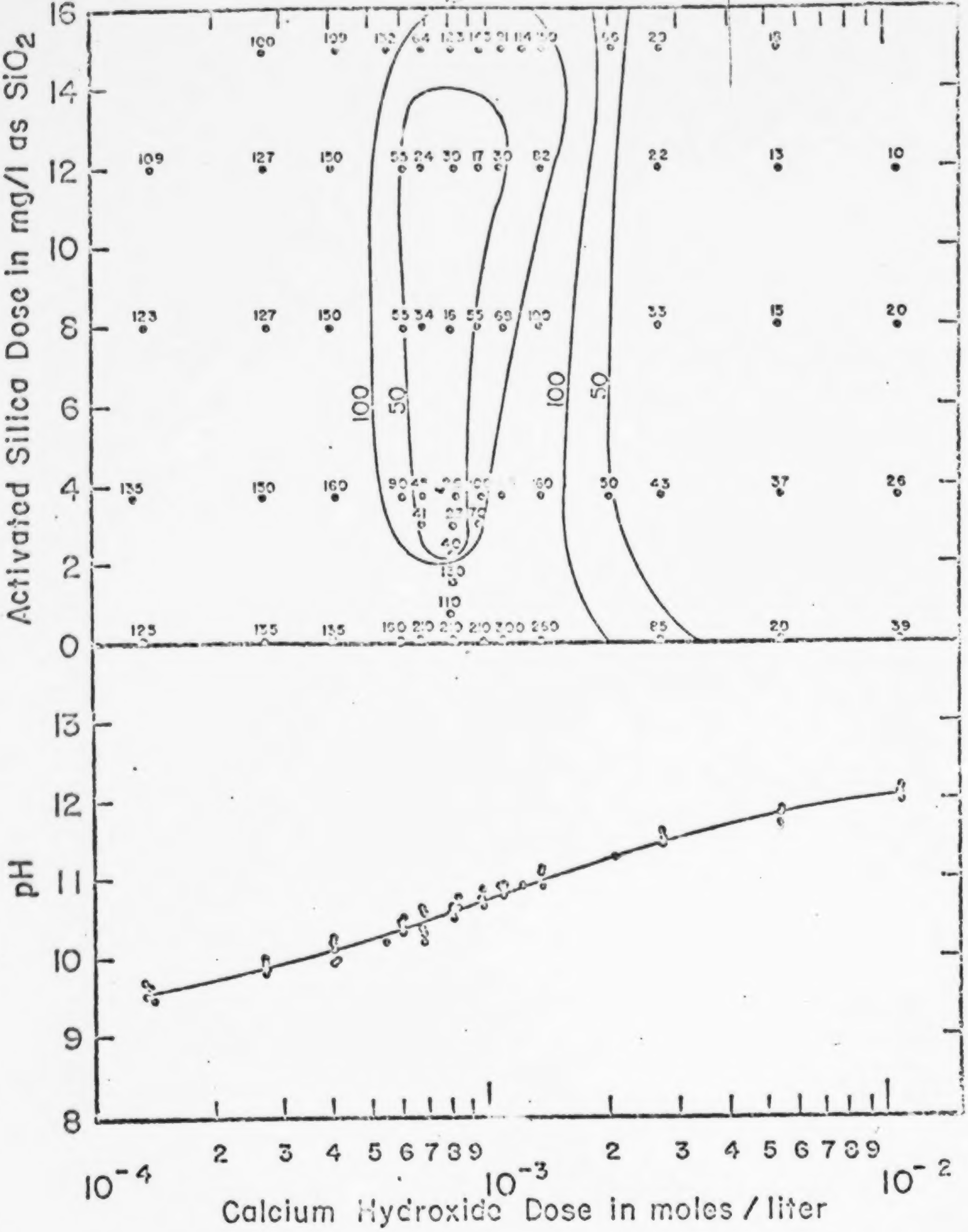

FIGURE V-1. RESIDUAL TURBIDITY CONTOURS FOR 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF ACTIVATED SILICA AND CALCIUM HYDROXIDE DOSES.

Resulting pH data are also shown as functions of calcium hydroxide dose. Turbidities are in Jackson Turbidity Units, JTU.

residual turbidity to 50% of its original value may be reduced from $3.5 \times 10^{-3}$ moles per liter to within the range of $6 \times 10^{-4}$ to $10^{-3}$ moles per liter when at least 2.0 mg/l but not more than 14.0 mg/l activated silica is used. Two interesting observations, which will be discussed later in more detail, are: 1) the upper limit of activated silica for effective clarification, and 2) the loss of effectiveness of activated silica at all concentrations when the lime dosage exceeds a certain level.

Figure V-2 shows the results of a similar study in which the test suspension contained 300 mg/l bentonite. The results are essentially the same as those for the 150 mg/l bentonite suspension, suggesting that the mechanism responsible for the favorable zone of coagulation is not influenced significantly by the concentration of the negatively charge colloidal bentonite, at least within the rather broad range studied.

A second type of suspension was prepared using 75 mg/l 5-micron Min-U-Sil. The results of a similar coagulation study with this suspension are shown in Figure V-3. The results observed are similar to those for the bentonite suspensions, except higher lime dosages (approximately 2 to 3 times as large) are required. It was also noted that settling time and completeness of

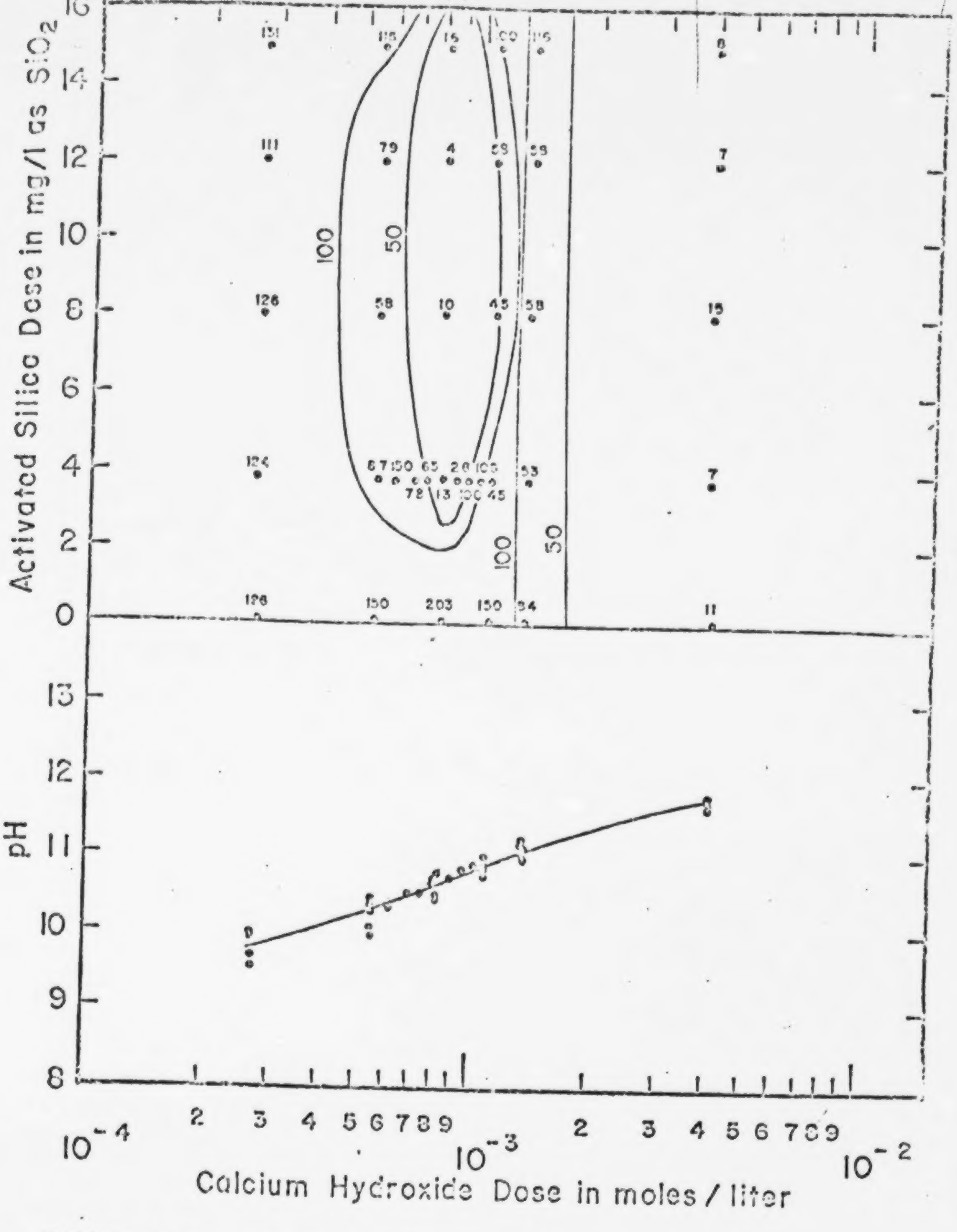

FIGURE V-2. RESIDUAL TURBIDITY CONTOURS FOR 300 mg/l BENTONITE IN $10^{-2}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF ACTIVATED SILICA AND CALCIUM HYDROXIDE DOSES.

Resulting pH data are also shown as functions of calcium hydroxide dose. Turbidities are Jackson Turbidity Units, JTU.

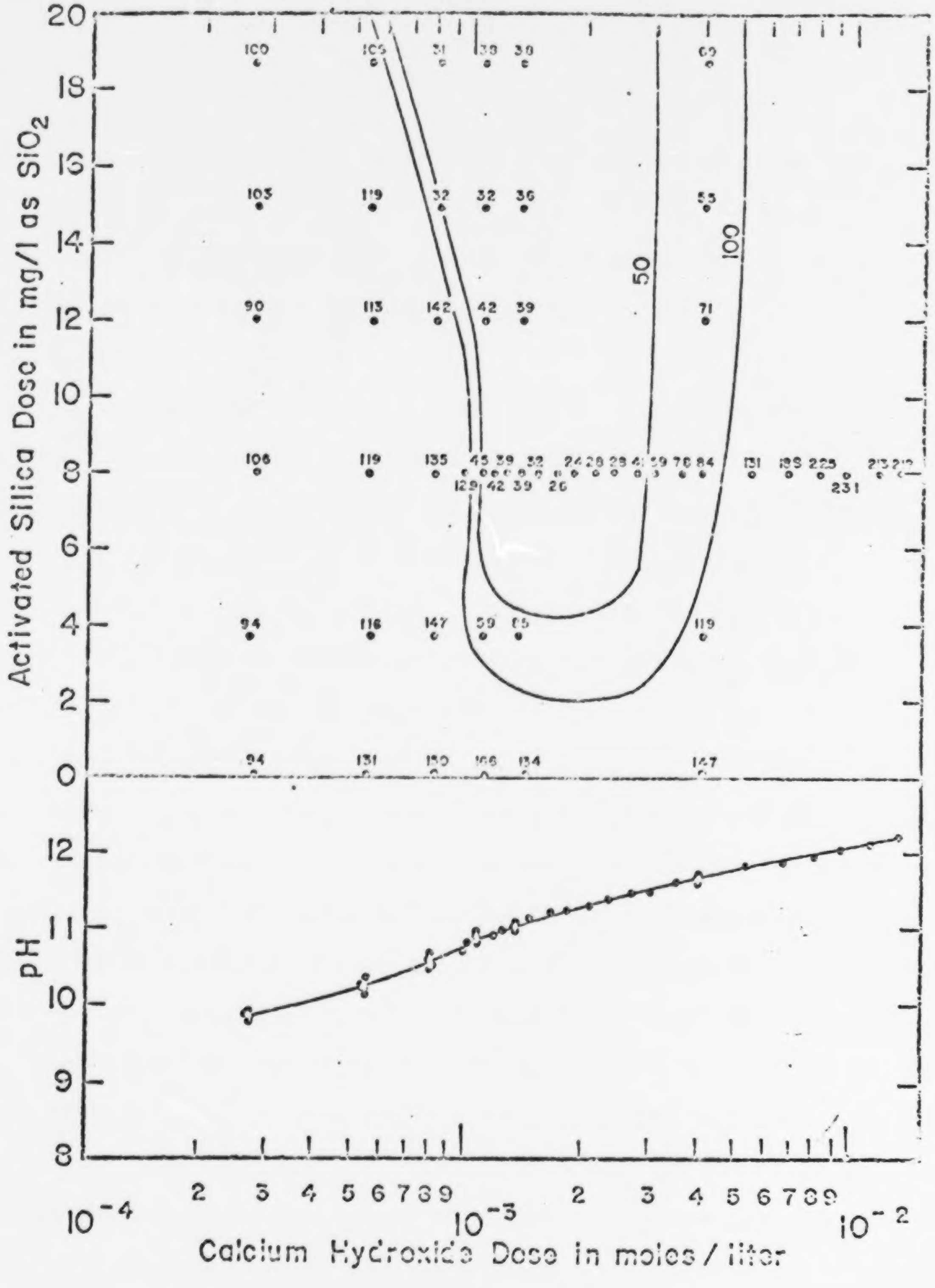

FIGURE V-3. RESIDUAL TURBIDITY CONTOURS FOR 75 mg/l 5-MICRON MIN-U-SIL IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF ACTIVATED SILICA AND CALCIUM HYDROXIDE DOSES.

Resulting pH data are also shown as functions of calcium hydroxide dose. Turbidities are in Jackson Turbidity Units, JTU.

clarification in the favorable zone of coagulation were not as good as for the bentonite suspensions. [illegible] activated silica clarification was not found even with lime dosages as high as $4 \times 10^{-3}$ moles per liter (300 mg/l $Ca(OH)_2$).

To compare the results observed above with a system containing no negatively charged colloids, a coagulation study was conducted on distilled water containing $10^{-3}$ moles per liter sodium bicarbonate, again using calcium hydroxide and activated silica. The results are shown in Figure V-4. Without activated silica, the residual turbidity increased with increasing lime dosage, indicating no significant loss of precipitated solids due to settling over the period of observation. The precipitated solids are calcium carbonate formed by the reaction between calcium and bicarbonate. In comparison, the bentonite suspension bentonite calcium carbonate particles are removed by high lime dosage. Slightly lower lime dosage is required for the suspension of higher bentonite concentration. In the case of the Min-U-Sil suspension, the Min-U-Sil calcium carbonate particles are not removed over the period of observation. This clarification phenomenon noted for the bentonite suspensions is not surprising as bentonite is frequently used as a coagulant aid. Its use results in a "weighting action" to permit rapid settling of iron and aluminum floc too light to settle rapidly. These

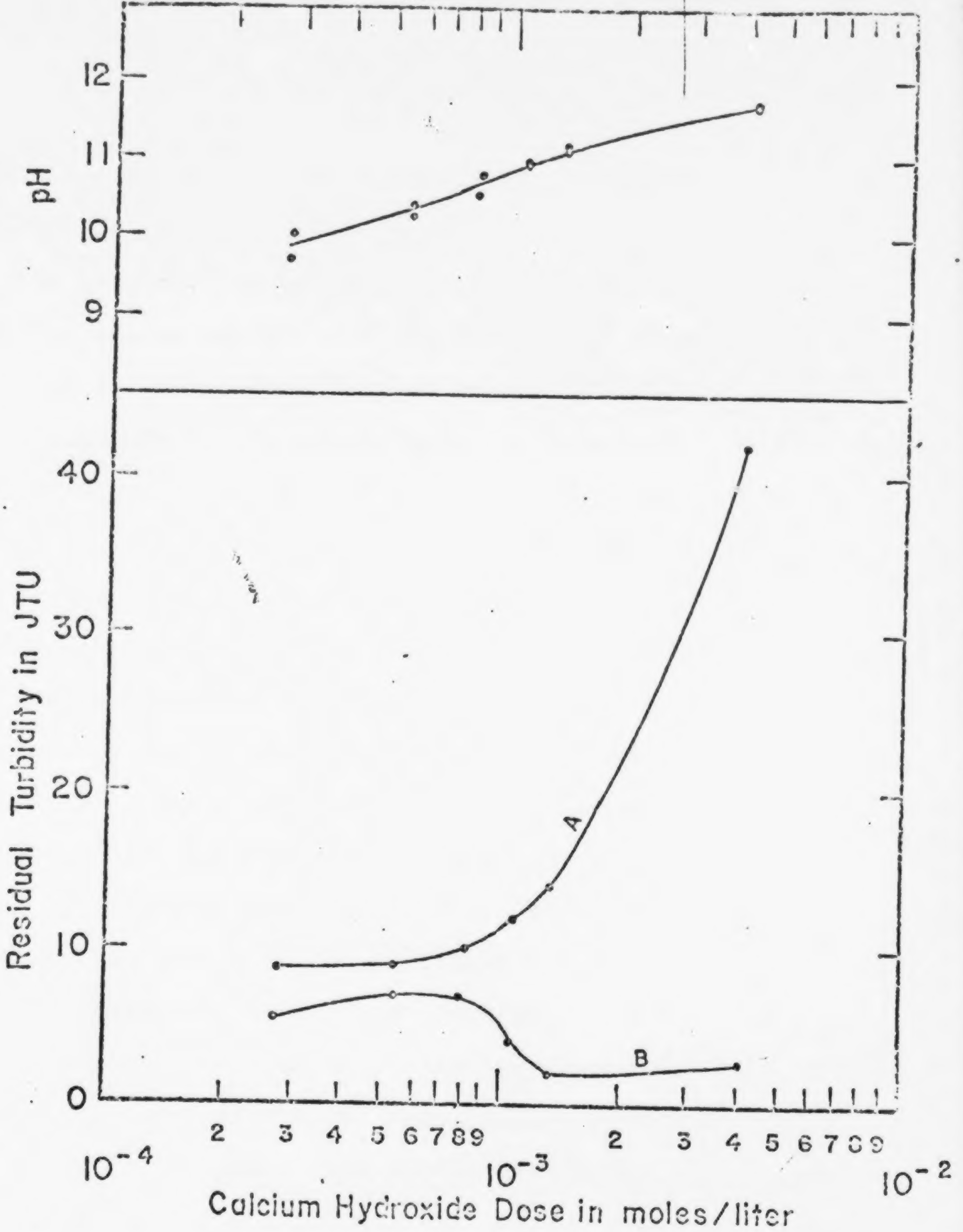

FIGURE V-4. RESIDUAL TURBIDITIES AND pH VALUES IN A $10^{-3}$ MOLAR SODIUM BICARBONATE SOLUTION AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE WITH AND WITHOUT ACTIVATED SILICA.

Curve A resulted from treatment with 5.63 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone. Resulting pH data are also shown as functions of calcium hydroxide dose.

iron and aluminum flocs are common when treating waters containing high color, low turbidity, and low mineral content. With activated silica however, residual turbidities of the sodium bicarbonate system dropped after the lime dosage exceeded about $10^{-3}$ moles per liter and remained low thereafter. In comparison, the bentonite suspensions required slightly less lime to accomplish clarification and the Min-U-Sil suspension required approximately the same, although the completeness of clarification was not as good for the Min-U-Sil suspension. The use of activated silica to treat these types of synthetic systems; bentonite, Min-U-Sil, and sodium bicarbonate alone; resulted in clarification and in the case of bentonite reduced significantly the required lime dosage. The loss of effectiveness of the activated silica at high lime dosage in the bentonite and Min-U-Sil suspensions is likely due to a charge reversal on the particles, or the high calcium concentration causes a change in the character of the activated silica resulting in loss of its effectiveness. The latter explanation is less likely since restabilization was not observed for the sodium bicarbonate system.

A synthetic mixture designed to simulate some of the characteristics frequently found in wastewaters was prepared to study the effects of lime and activated silica

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on wastewater coagulation-sedimentation processes. The composition of this mixture is described in Table V-1. Kjeldahl nitrogen, total phosphate, and COD analyses were made with a Technicon Auto Analyzer according to the procedures included in the Appendix. As indicated by the data presented in Figure V-5, clarification was accomplished with significantly less lime than was required for the bentonite-sodium bicarbonate system, the data for which has been presented in Figure V-1. Activated silica exhibited little effect except to increase the lime requirement slightly. This increase appeared to be independent of the concentration of silica over the range studied (3.75 to 15.0 mg/l $SiO_2$).

Analyses of Kjeldahl nitrogen and COD indicated that neither is removed to any significant extent by this treatment technique. Total phosphate however, was found to be removed almost completely by addition of $10^{-3}$ moles per liter calcium hydroxide. This removal, as shown in Figure V-5, is independent of activated silica concentration. The effect of calcium hydroxide addition on pH is also shown in Figure V-5 to be essentially independent of activated silica concentration. The reason for the low lime dosage required for clarification and the possibility of clarification without the use of lime appears to be due to the presence of phosphate, which

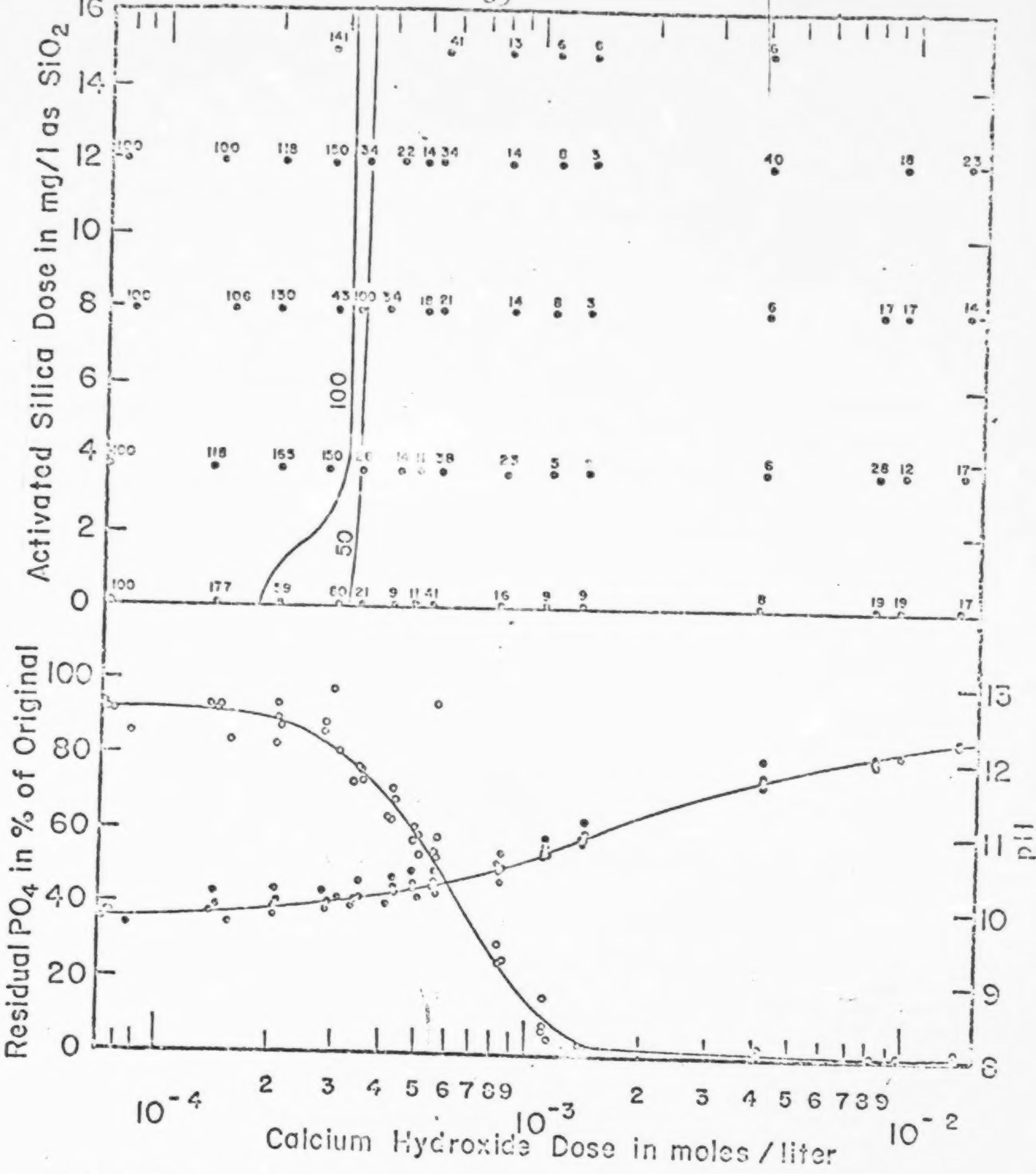

FIGURE V-5. RESIDUAL TURBIDITY CONTOURS FOR SYNTHETIC MIXED WASTEWATER AS FUNCTIONS OF ACTIVATED SILICA AND CALCIUM HYDROXIDE DOSES.

Composition of the synthetic mixed wastewater is shown in Table V-1. Resulting pH data are represented by solid circles and the right ordinate and resulting phosphate concentration data are represented by open circles and the left ordinate in the lower portion of the figure. Turbidities are in Jackson Turbidity Units, JTU.

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precipitates as hydroxylapatite. This effect was studied in detail and the results reported in a later section.

TABLE V-1

SYNTHETIC MIXED WASTEWATER

| Component | Concentration** |
|---|---|
| Negatively Charged Colloid | |
| Bentonite | 150 mg/l |
| Carbonate Buffer | |
| Sodium Bicarbonate, $NaHCO_3$ | $10^{-3}$ |
| Dissolved Organics* | |
| Phenol, $C_6H_5OH$ | $7.82 \times 10^{-4}$ |
| Sodium Acetate, $NaC_2H_3O_2$ | $8.96 \times 10^{-4}$ |
| Sodium Lauryl Sulfate, $CH_3(CH_2)_{11}OSO_3Na$ | $4.26 \times 10^{-5}$ |
| n-Hexanol, $CH_3(CH_2)_5OH$ | $1.20 \times 10^{-5}$ |
| Organic Nitrogen | |
| Urea, $NH_2CONH_2$ | $2.14 \times 10^{-3}$ |
| Phosphate | |
| Disodium Hydrogen Phosphate, $Na_2HPO_4$ | $4.85 \times 10^{-4}$ |

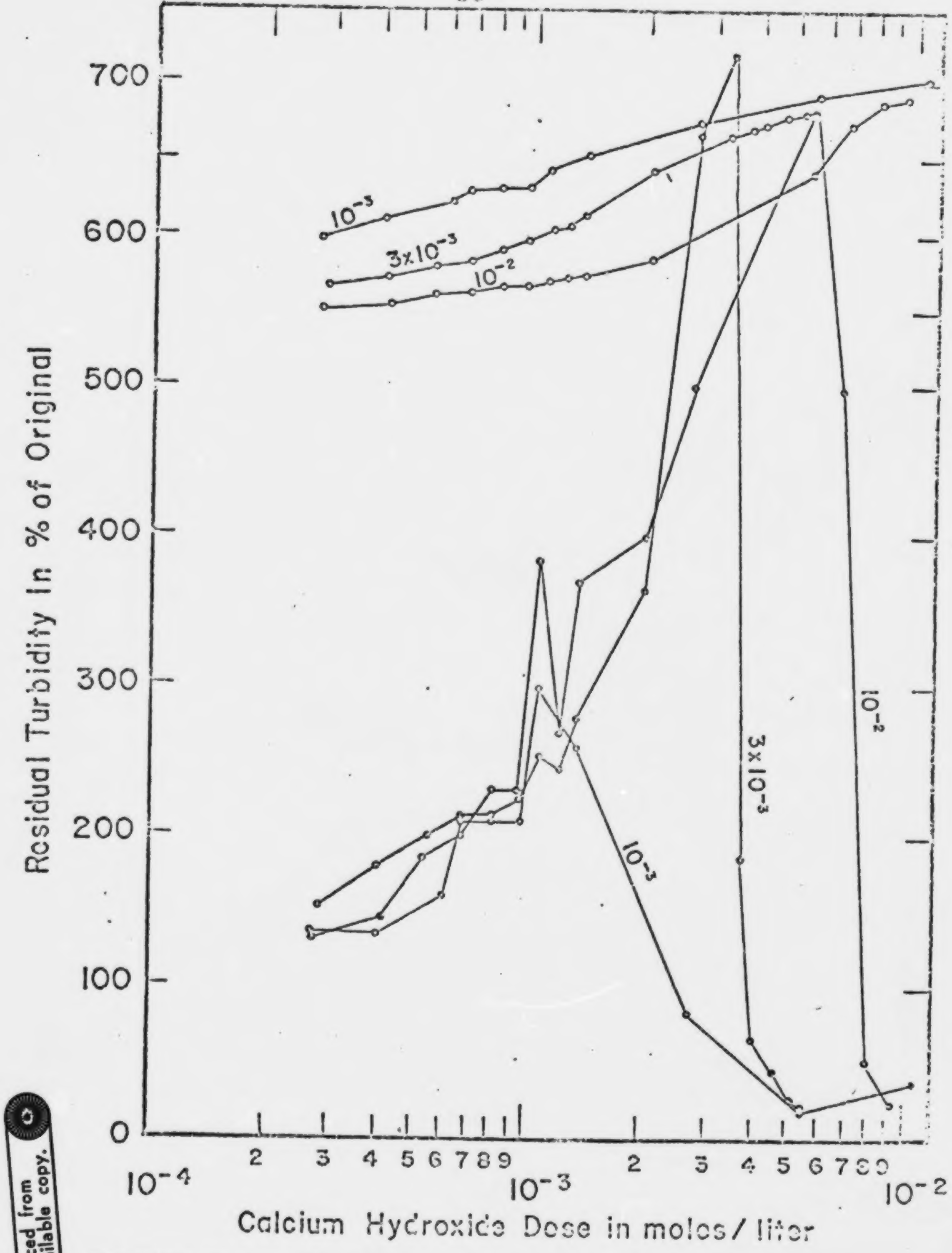
*Found to exhibit a COD of 200 mg/l

**Moles per liter except where otherwise indicated.

Effect of Alkalinity.

Following coagulation studies of raw sewages, described in detail in the following chapter, it appeared that either high alkalinity or low pH was the cause for the loss of effectiveness of activated silica in reducing the lime required to treat these sewages. The results of these studies are shown in the following chapter Figures VI-1 and VI-2. A number of coagulation studies of synthetic systems using 150 mg/1 bentonite in solutions of varying sodium bicarbonate concentration were conducted and the results are discussed in the following paragraphs.

Figure V-6 indicates lime requirements for clarification of a 150 mg/1 bentonite suspension for different alkalinities, without the use of activated silica. As alkalinity, in the form of sodium bicarbonate, was increased from $10^{-3}$, to $3 \times 10^{-3}$, and to $10^{-2}$ moles per liter the calcium hydroxide concentration required to halve the original turbidity, $D_{t/2}$, was increased from $3.9 \times 10^{-3}$ to $4.4 \times 10^{-3}$ and to $8.1 \times 10^{-3}$, respectively. Varying pH as a function of calcium hydroxide concentration is also shown in this figure. The results of a study of a 150 mg/1 bentonite suspension with alkalinities ranging from $5 \times 10^{-4}$ to $10^{-2}$ moles per liter of sodium bicarbonate are shown in Figure V-7. In this case activated silica was used. At the lowest level of alkalinity, clarification was observed



FIGURES V-6. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE AND INITIAL SODIUM BICARBONATE CONCENTRATION.

Turbidities are represented by solid circles and the left ordinate and pH values by open circles and the right ordinate. Sodium bicarbonate concentrations are $10^{-3}$, $3 \times 10^{-3}$, and $10^{-2}$ moles per liter as shown in the figure.

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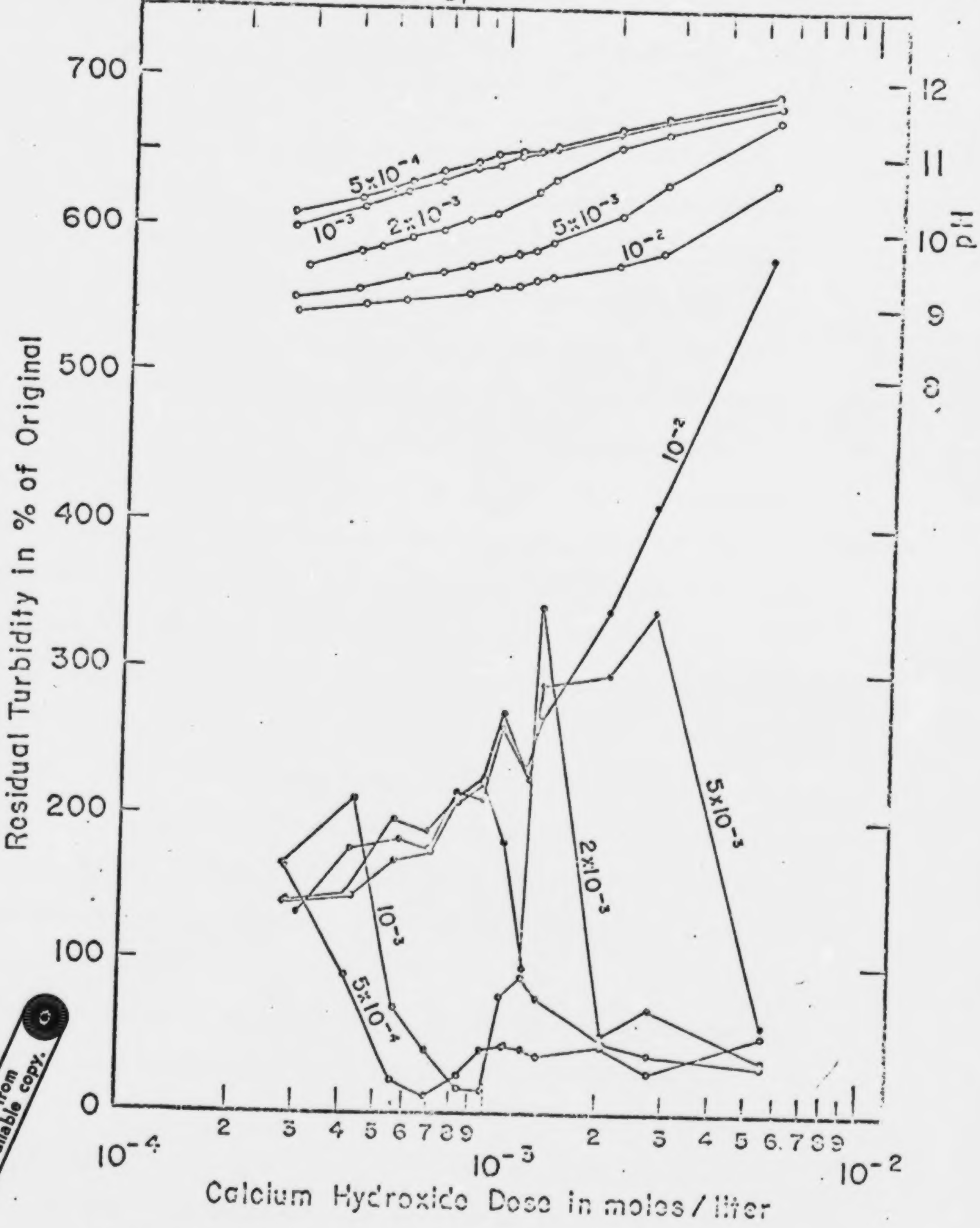

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FIGURE V-7. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE WITH 3.75 mg/l (as $SiO_2$) ACTIVATED SILICA AND INITIAL SODIUM BICARBONATE CONCENTRATION.

Turbidities are represented by solid circles and the left ordinate and pH values by open circles and the right ordinate. Sodium bicarbonate concentrations are 5 x $10^{-4}$, $10^{-3}$, 2 x $10^{-3}$, 5 x $10^{-3}$, and $10^{-2}$ moles per liter, as shown in the figure.

with very low lime addition and remained effective at even higher lime additions. With increasing alkalinity lime requirement increased and an effective zone of clarification developed, above which increased lime additions resulted in a loss of effectiveness. At even higher lime additions the results were similar to those when activated silica was not used. This effective zone of coagulation continued to narrow with increasing alkalinity until at high levels of alkalinity it was lost and clarification was not found until lime additions reached the high levels required without the use of activated silica. Figure V-8 shows the results of a study similar to that discussed above, except the activated silica concentration was increased from 3.75 to 8.0 mg/l $SiO_2$. No significant change was observed. Further increase of activated silica to 18 mg/l $SiO_2$ was ineffective in clarification of the high alkalinity suspensions as shown in Figure V-9.

The results of a study in which sodium bicarbonate levels in 150 mg/l bentonite suspensions were varied throughout the range of $10^{-4}$ to $10^{-2}$ moles per liter and treatment was provided using constant concentrations of lime and activated silica are shown in Figure V-10. In all these cases, the activated silica was observed to be ineffective whenever the sodium bicarbonate con-

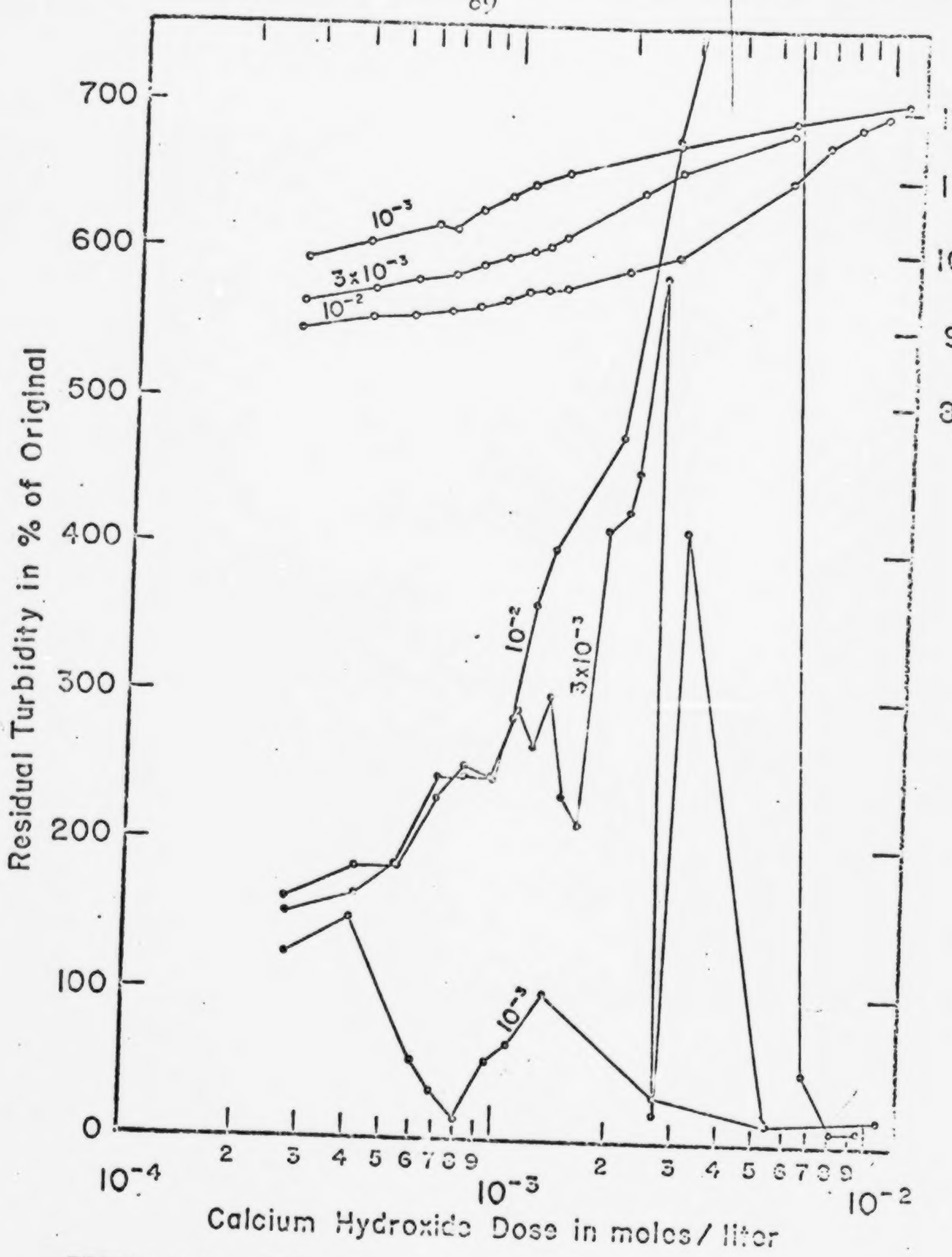

FIGURE V-8. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/1 BENTONITE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE USED WITH 8.0 mg/1 (as $SiO_2$) ACTIVATED SILICA AND INITIAL SODIUM BICARBONATE CONCENTRATION.

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Turbidities are represented by solid circles and the left ordinate and pH values by open circles and the right ordinate. Sodium bicarbonate concentrations are $10^{-3}$, $3 \times 10^{-3}$, and $10^{-2}$ moles per liter, as shown in the figure.

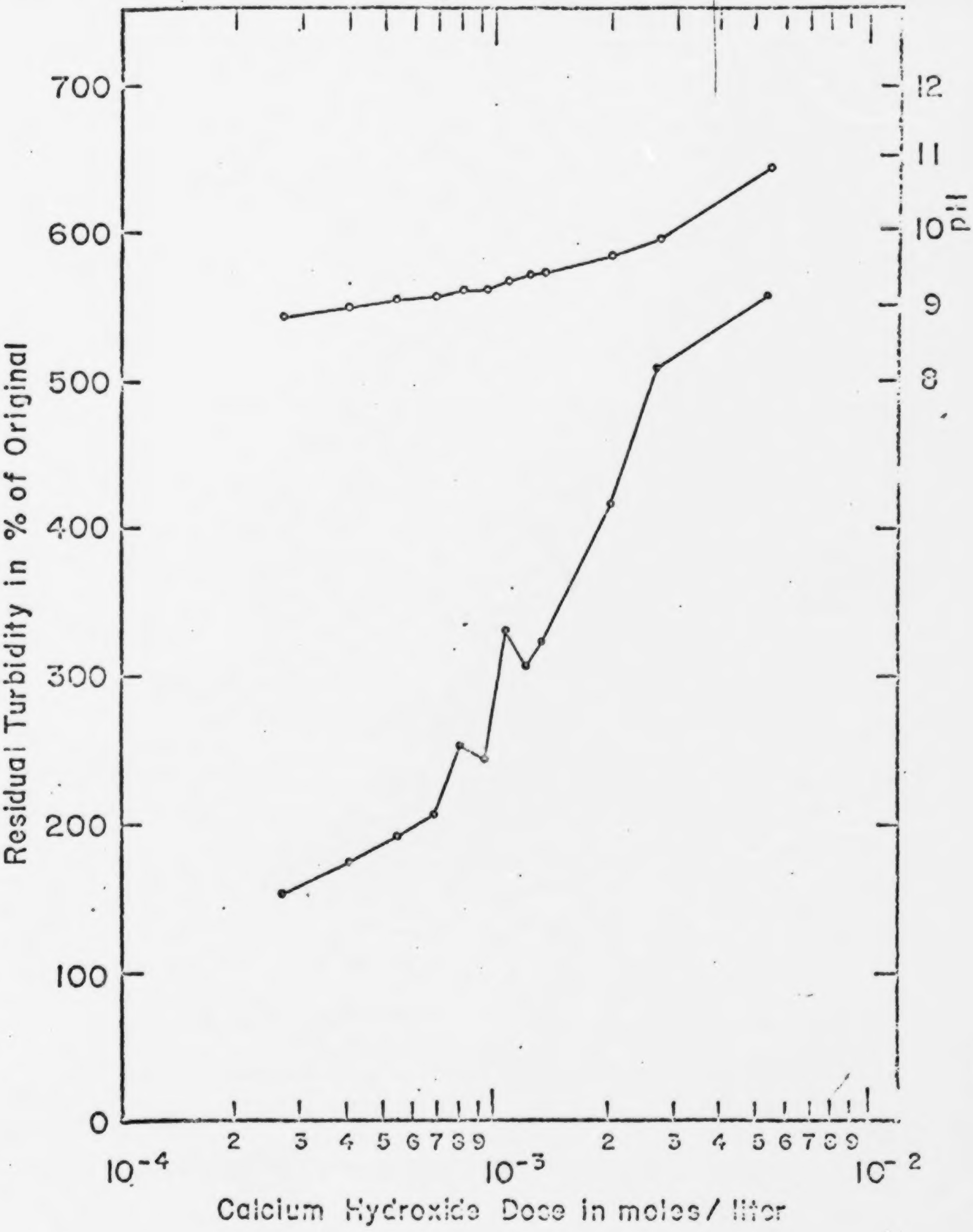

FIGURE V-9. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE IN $10^{-2}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE WITH 18.0 mg/l (as $SiO_2$) ACTIVATED SILICA.

Turbidities are represented by solid circles and the left ordinate and pH values by open circles and the right ordinate.

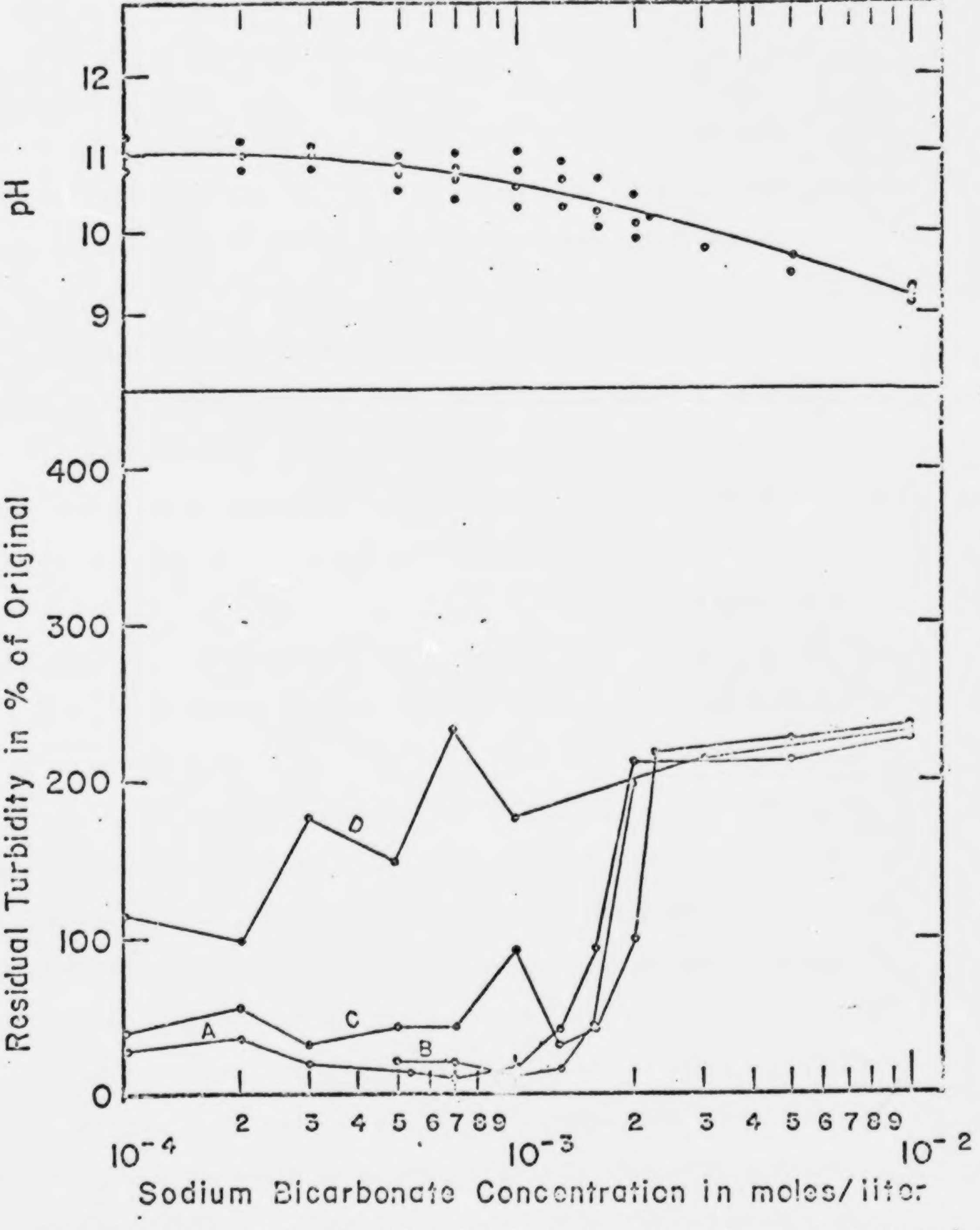

FIGURE V-10. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE AS FUNCTIONS OF INITIAL SODIUM BICARBONATE CONCENTRATION AND ACTIVATED SILICA AND CALCIUM HYDROXIDE DOSES.

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Curve A resulted from treatment using 8.1 x $10^{-4}$ moles per liter calcium hydroxide plus 3.75 mg/l (as $SiO_2$) activated silica, Curve B from 8.1 x $10^{-4}$ moles per liter calcium hydroxide plus 12.0 mg/l activated silica, Curve C from 1.23 x $10^{-3}$ moles per liter calcium hydroxide plus 3.75 mg/l activated silica, and Curve D from 8.1 x $10^{-4}$ moles per liter calcium hydroxide.

centration exceeded about 1.5 x $10^{-3}$ moles per liter.

Effects of ionic strength resulting from increase sodium bicarbonate concentration were demonstrated to be negligibleas shown in Figures V-11 and V-12. Bentonite suspensions of 150 mg/l in 5 x $10^{-4}$ and $10^{-3}$ molar sodium bicarbonate solutions which contained sufficient sodium chloride to increase the ionic strength to $10^{-2}$ molar were studied, and the results compared to those containing $10^{-2}$, 5 x $10^{-4}$, and $10^{-3}$ molar sodium bicarbonate. In these comparisons it was found that the behavior of the bentonite suspensions was primarily affected by sodium bicarbonate concentration, and not ionic strength.

In an attempt to separate the effects of pH and calcium concentration, calcium hydroxide additions were replaced with calcium nitrate alone or together with sulfuric acid or sodium hydroxide to vary pH independently of calcium concentration. These combinations of chemicals together with activated silica were studied with 150 mg/l molar sodium bicarbonate solutions. The results are shown in Figure V-13 in terms of calcium concentrations required to halve the original turbidity, $D_{t/2}$, as a function of pH for the three levels of alkalinity. Parallel studies were carried out with no activated silica at a concentration of 3.75 mg/l $SiO_2$. It was found that

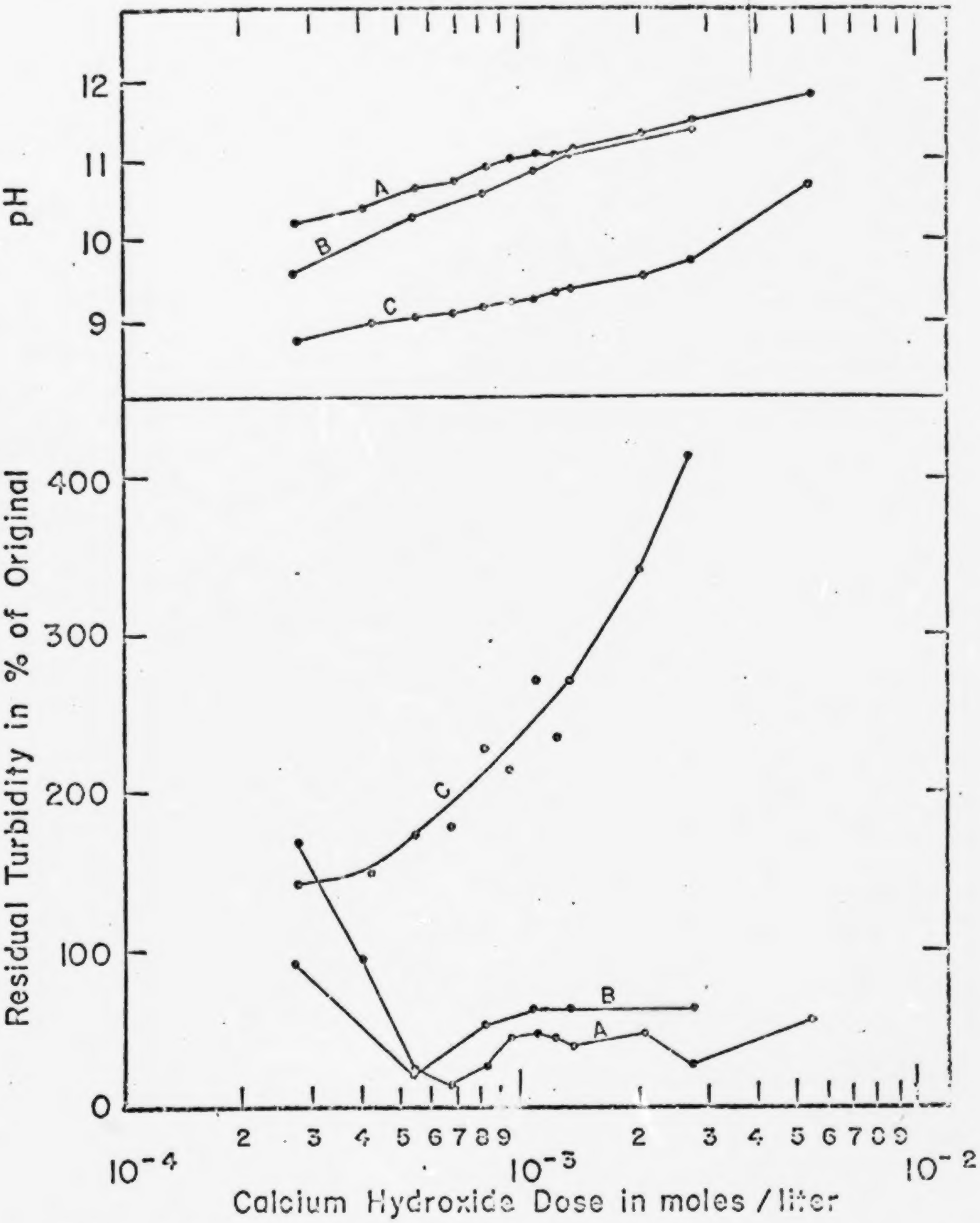

FIGURE V-11. EFFECT OF IONIC STRENGTH ON RESIDUAL TURBIDITY AND pH OF 150 mg/1 BENTONITE IN $5 \times 10^{-4}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE WITH 3.75 mg/1 (as $SiO_2$) ACTIVATED SILICA.

Curve A resulted from $5 \times 10^{-4}$ molar sodium bicarbonate, Curve B from $5 \times 10^{-4}$ molar sodium bicarbonate plus $9.5 \times 10^{-4}$ molar sodium chloride, and Curve C from $10^{-2}$ molar sodium bicarbonate.

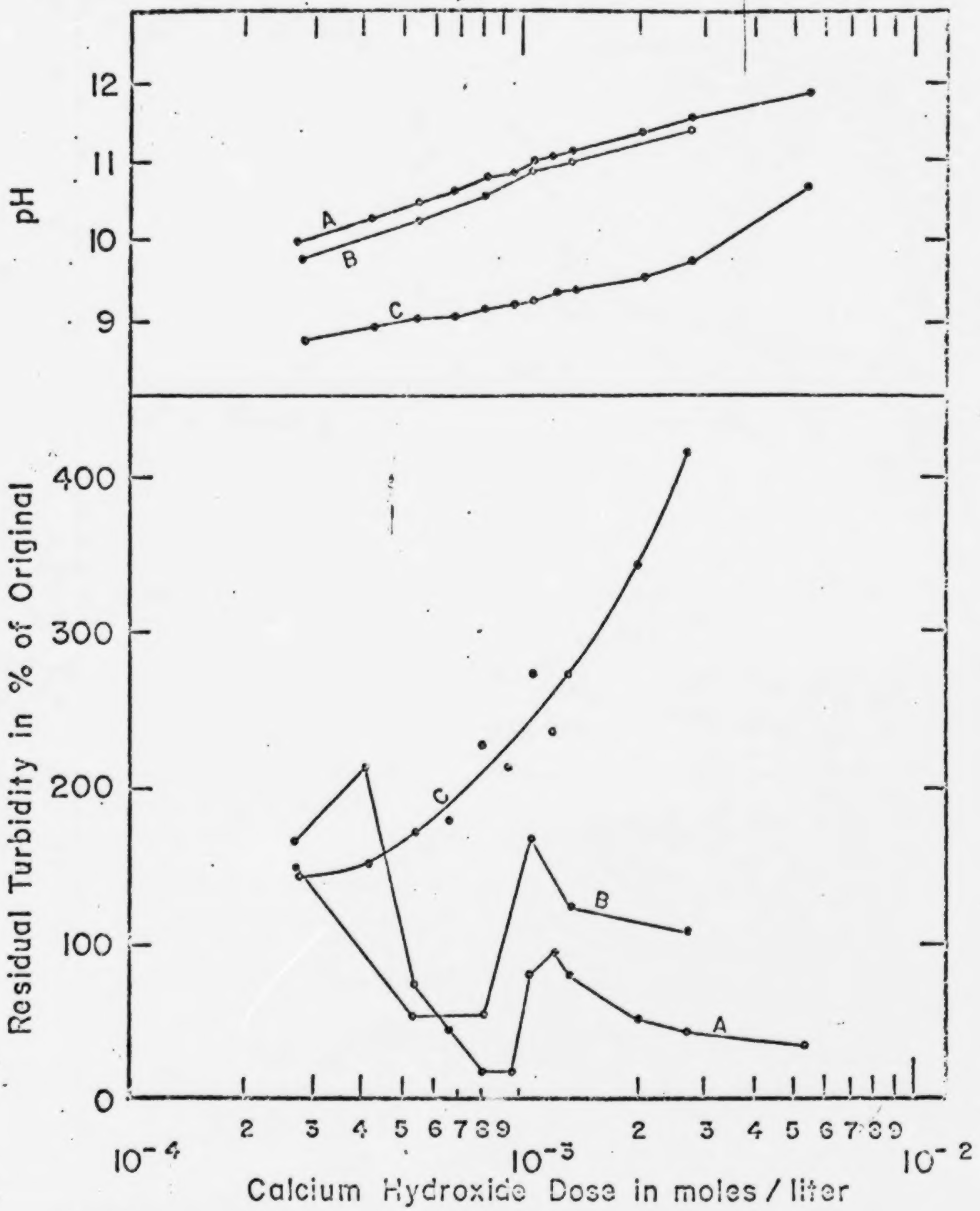

FIGURE V-12. EFFECT OF IONIC STRENGTH ON RESIDUAL TURBIDITY AND pH of 150 mg/1 BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE WITH 3.75 mg/1 (as $SiO_2$) ACTIVATED SILICA.

Curve A resulted from $10^{-3}$ molar sodium bicarbonate, Curve B from $10^{-3}$ molar sodium bicarbonate plus 9.0 x $10^{-3}$ molar sodium chloride, and Curve C from $10^{-2}$ molar sodium bicarbonate.

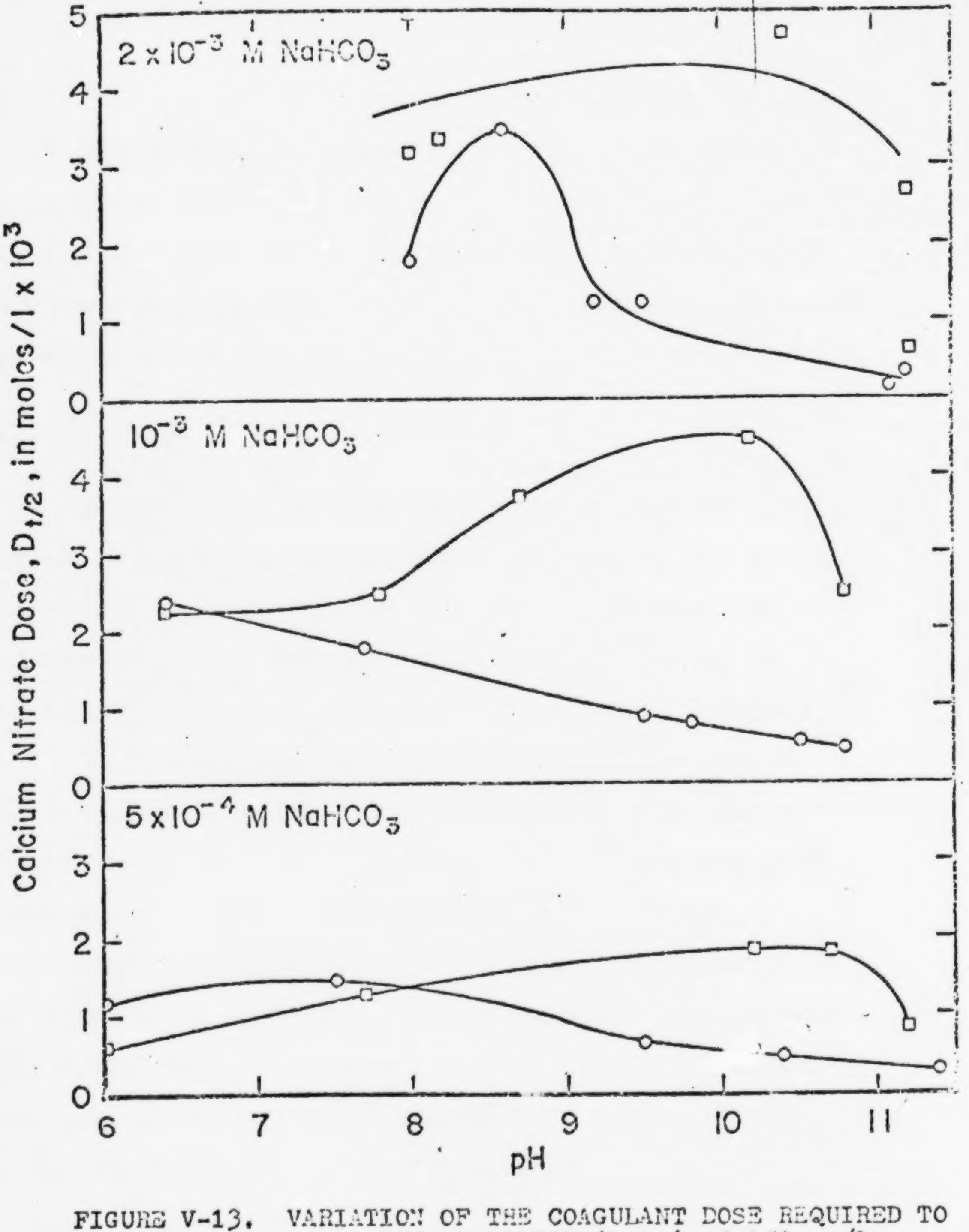

FIGURE V-13. VARIATION OF THE COAGULANT DOSE REQUIRED TO HALVE THE TURBIDITY ($D_{t/2}$) of 150 mg/l BENTONITE SOLUTIONS AS FUNCTIONS OF INITIAL SODIUM BICARBONATE CONCENTRATION, pH, AND CALCIUM NITRATE DOSE WITH 3.75 mg/l (as $SiO_2$) ACTIVATED SILICA.

Sulfuric acid or sodium hydroxide added with calcium nitrate provided variation in pH values. Results of treatment with calcium nitrate and activated silica are represented by circles and treatment with calcium nitrate alone by squares.

above pH 9 the calcium nitrate requirement was essentially independent of pH and significantly less when activated silica was used. At lower pH values, a condition not likely when lime is used on low alkalinity wastewaters, the reduction in calcium nitrate requirement accomplished by activated silica is less significant, or non existent.

Effect of pH.

The effect of calcium concentration, rather than pH, appeared to be the significant factor in the use of lime as a coagulant in the experimental systems, as discussed above. Further studies were conducted in an attempt to better define this observation. First a 150 mg/l bentonite suspension in $10^{-3}$ molar sodium carbonate was studied. The results show this system to behave similar to a comparable system prepared with sodium bicarbonate. This similarity can be seen by the curves in Figure V-14 and the appropriate curves in Figures V-6 and V-7. It is significant to note that the sodium carbonate system, although equal in carbonate species, has an alkalinity twice that of the sodium bicarbonate system, along with a higher pH.

Since addition of lime to high alkalinity wastewaters results in lower residual pH than when added to low alkalinity wastewaters, it was decided to reduce the pH by using a noncarbonate buffer. Sodium borate was

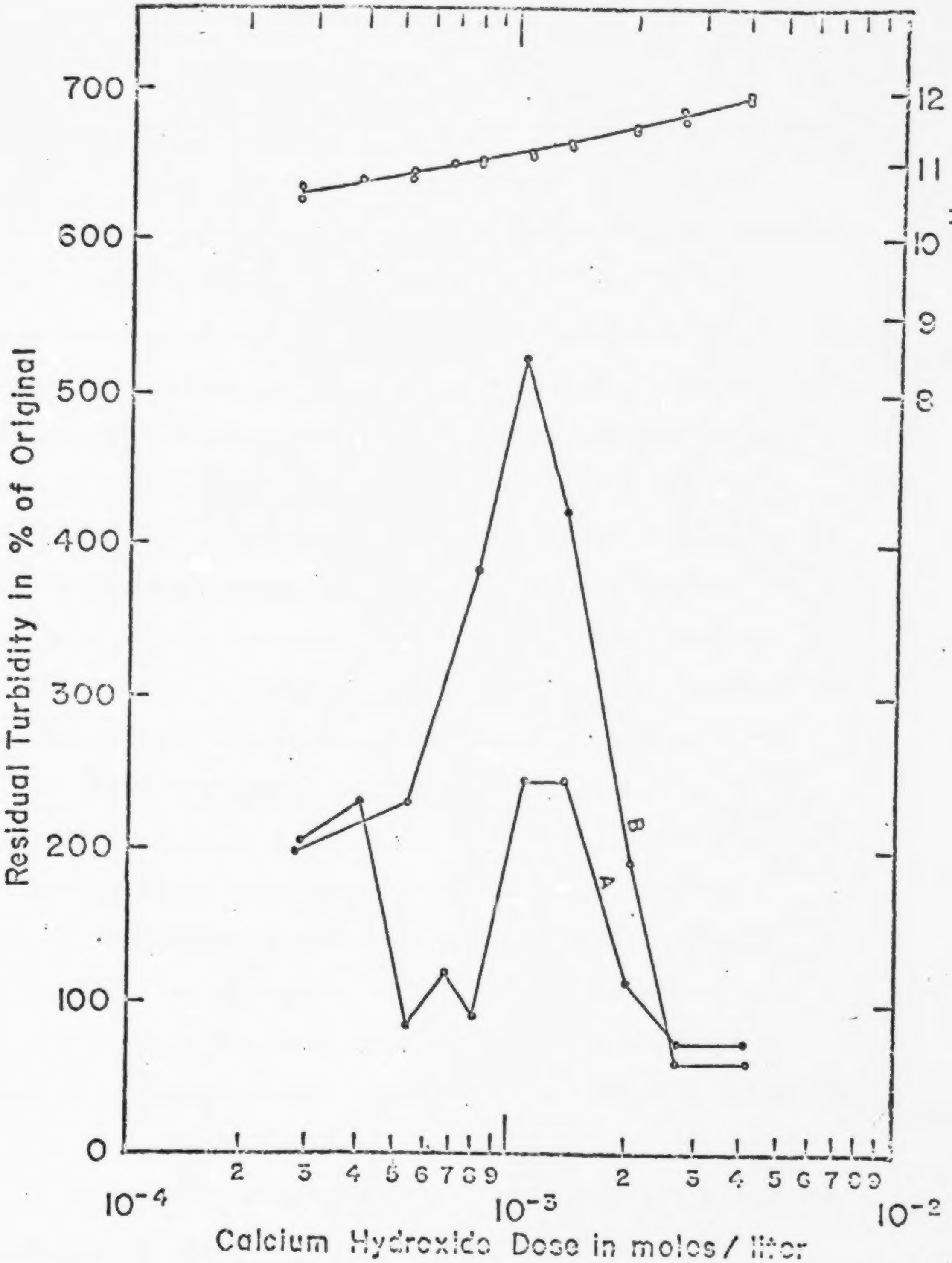

FIGURE V-14. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM CARBONATE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE.

Turbidities are shown by solid circles and the left hand ordinate and pH values by open circles and the right hand ordinate. Curve A resulted from treatment with 3.75 mg/l as ($SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

chosen for this purpose. Suspensions of 150 mg/l bentonite in four different solutions were studied, these were: 1) $10^{-3}$ molar sodium borate which provided a borate control; 2) $10^{-3}$ molar sodium bicarbonate plus $10^{-3}$ molar sodium borate which provided the $10^{-3}$ molar bicarbonate concentration studied extensively in the systems reported in the preceding sections, but a lower residual pH due to the buffering effect of the borate; 3) the same solutions as 2) above, except $7.5 \times 10^{-4}$ moles per liter of sulfuric acid were added to further reduce the residual pH; and 4) also the same as 2) above, except $1.5 \times 10^{-3}$ moles per liter of sulfuric acid were added to provide a very low residual pH. The results are shown in Figures V-15 through V-18 for the above systems 1) through 4), respectively. In all these systems without the use of activated silica, calcium hydroxide requirements were similar to those found in the sodium bicarbonate system shown on Figure V-6 although the pH values were lower. When activated silica was used, the lime requirements when compared to Figure V-7, indicate only slightly higher calcium hydroxide dosages to halve the original turbidity, $D_{t/2}$, although the pH ranged from approximately 8 in the system including sodium borate and the high acid concentration to almost 11 when only sodium bicarbonate was used..

Results of a detail study to demonstrate the effect

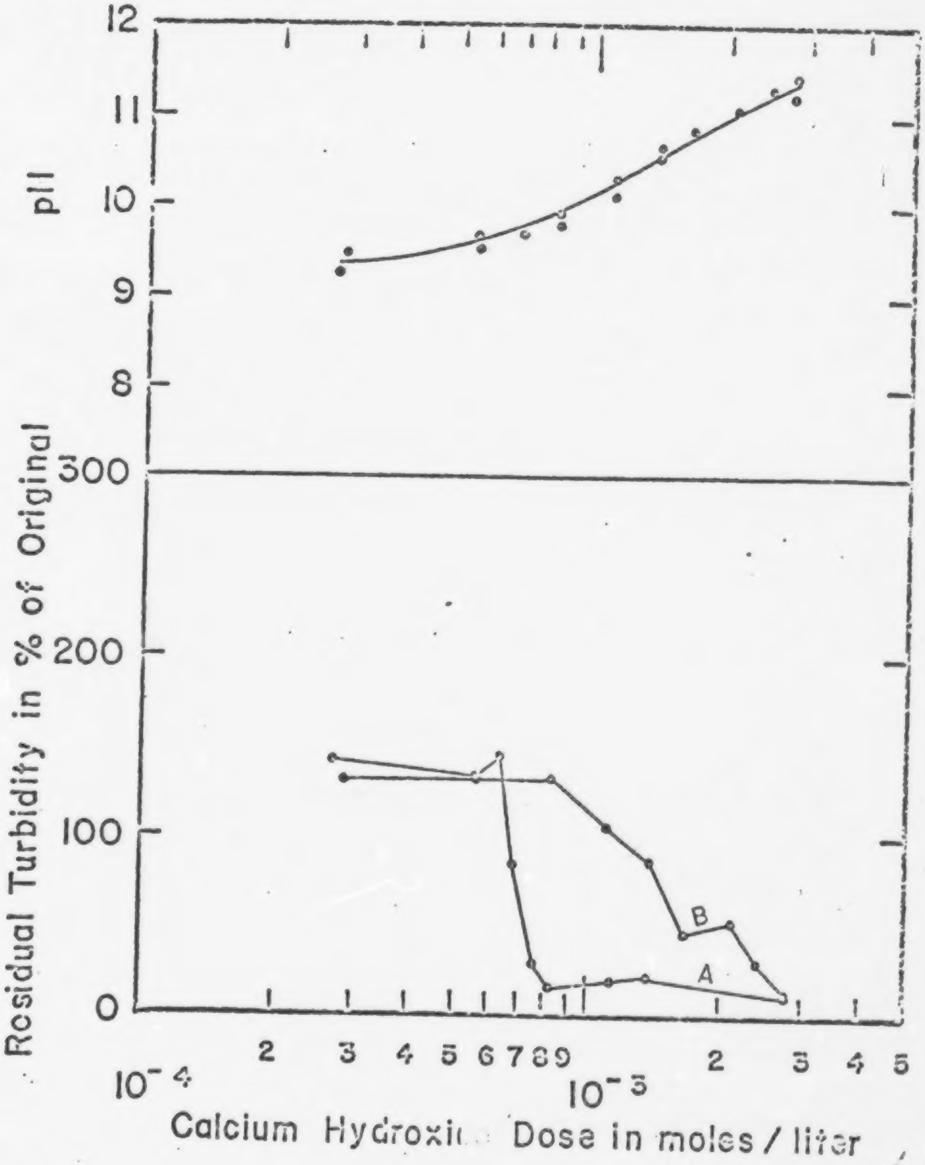

FIGURE V-15. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BORATE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE.

Curve A resulted from treatment with 3.75 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone. .

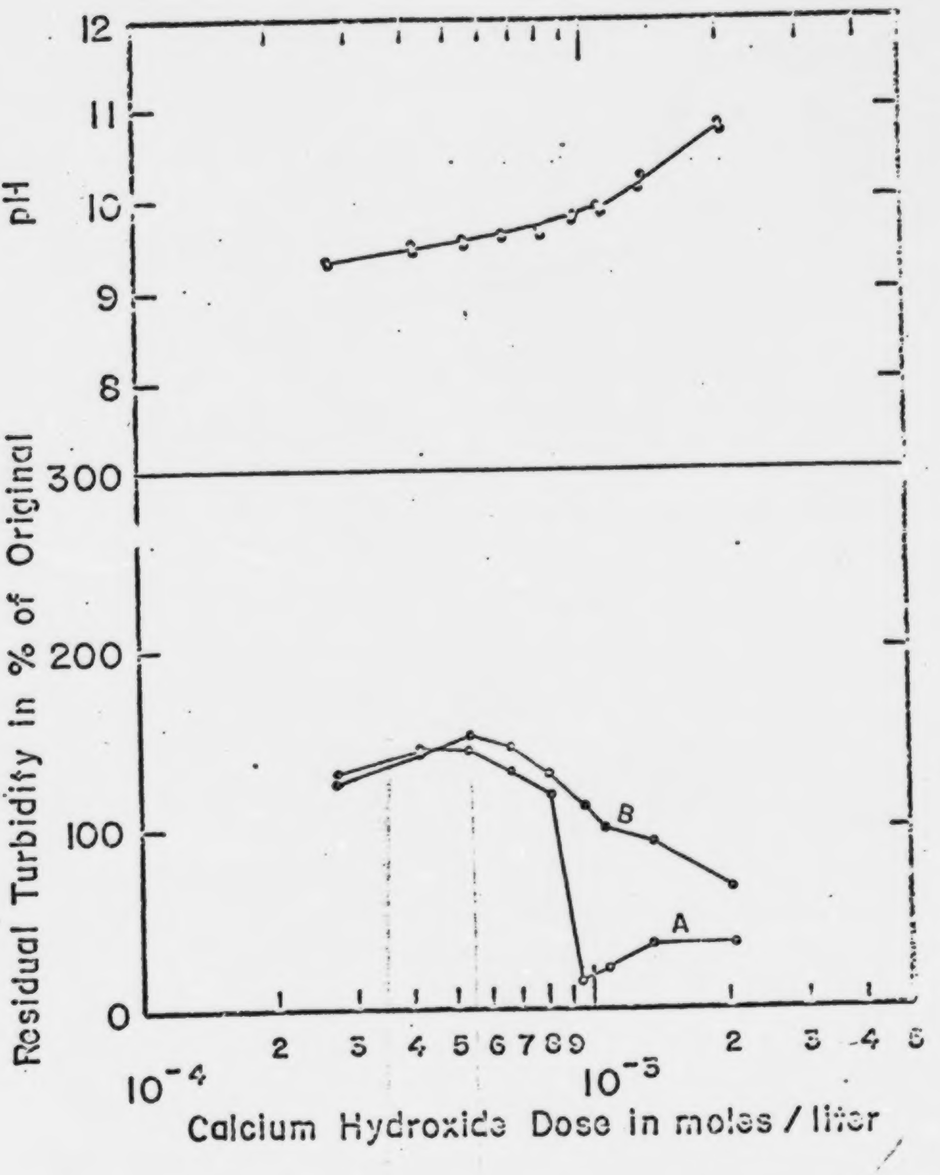

FIGURE V-16. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BORATE AND $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE.

Curve A resulted from treatment with 3.75 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

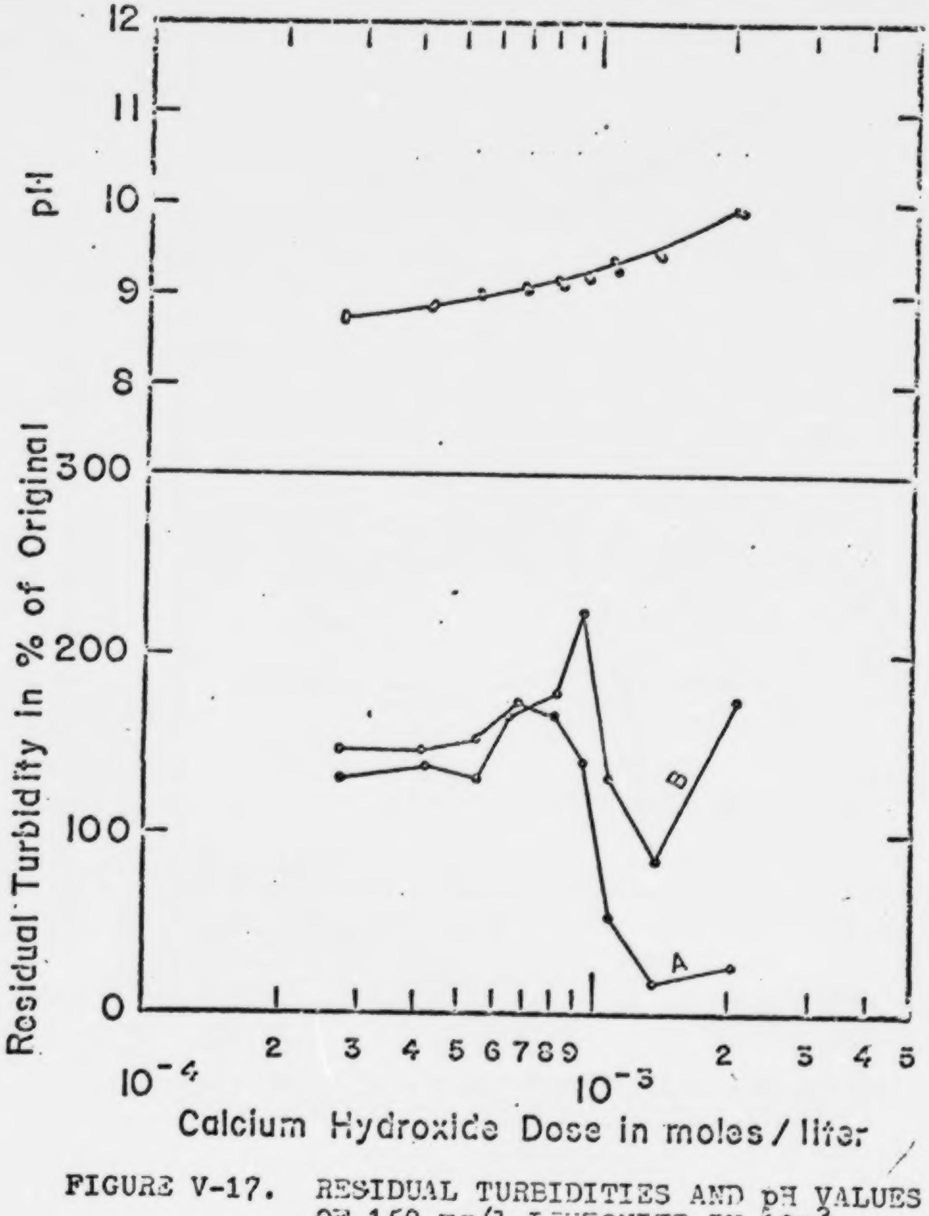

FIGURE V-17. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/1 BENTONITE IN $10^{-3}$ MOLAR SODIUM BORATE, $10^{-3}$ MOLAR SODIUM BICARBONATE, AND $7.5 \times 10^{-4}$ MOLAR SULFURIC ACID AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE.

Curve A resulted from treatment with 3.75 mg/1 (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

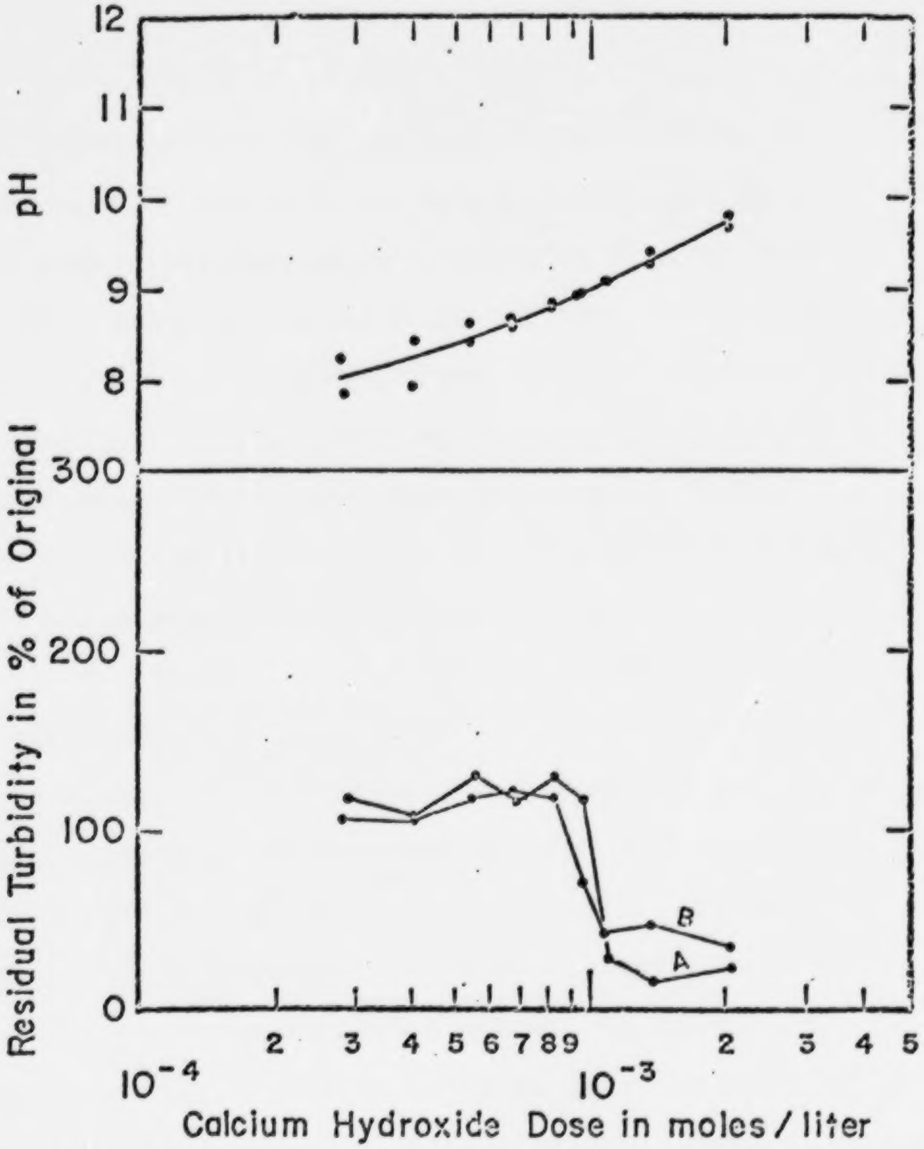

FIGURE V-18. RESIDUAL TURBIDITIES AND pH VALUES OF 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BORATE, $10^{-3}$ MOLAR SODIUM BICARBONATE, AND $1.5 \times 10^{-3}$ MOLAR SULFURIC ACID AS FUNCTIONS OF CALCIUM HYDROXIDE DOSE.

Curve A resulted from treatment with 3.75 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

of pH, activated silica, and calcium concentrations on clarifications of a 150 mg/l bentonite suspension in $10^{-3}$ molar sodium bicarbonate are shown in Figures V-19 through V-22. Calcium was added in the form of calcium nitrate alone, with sodium hydroxide, or with sulfuric acid for pH adjustment in place of calcium hydroxide. The zones of effective coagulation are shown. Without activated silica clarification is not accomplished below $2.5 \times 10^{-3}$ moles per liter of calcium at any of the pH values studied. Above $2.5 \times 10^{-3}$ molar calcium clarification begins to be accomplished but settling was noted to be slow, floc size small, and completeness of clarification poor as demonstrated by the erratic and often high turbidity values above this level. Below pH 8 no significant reduction in calcium requirement was observed when using activated silica. In fact, the requirement for calcium was observed to increase with increasing activated silica additions in this region. Above pH 8 significant calcium reductions were observed using activated silica in any of the three concentrations studied (3.75, 8.0, and 12.0 mg/l $SiO_2$) and this reduction was greater with increased pH. At very high pH values, approximately 11 and greater, activated silica appeared to have little benefit in clarification when the calcium dosage was also high. This is likely due to the charge

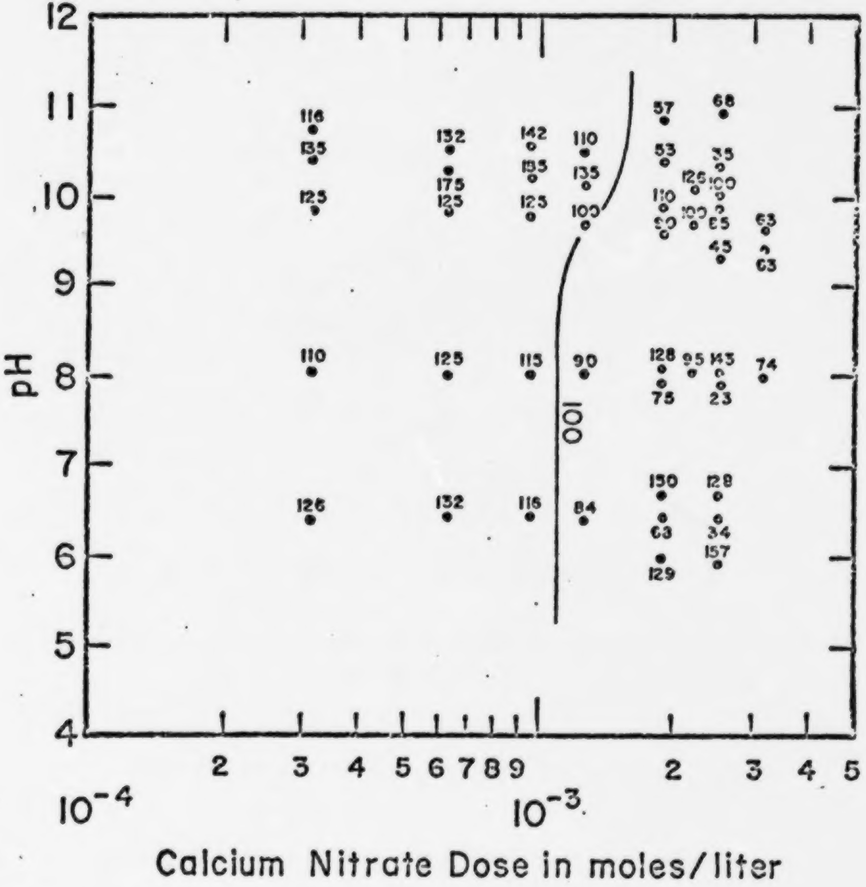

FIGURE V-19. RESIDUAL TURBIDITY CONTOURS FOR 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF pH AND CALCIUM NITRATE DOSE.

Sulfuric acid or sodium hydroxide added with calcium nitrate provided variation in pH values. Turbidities are in Jackson Turbidity Units, JTU.

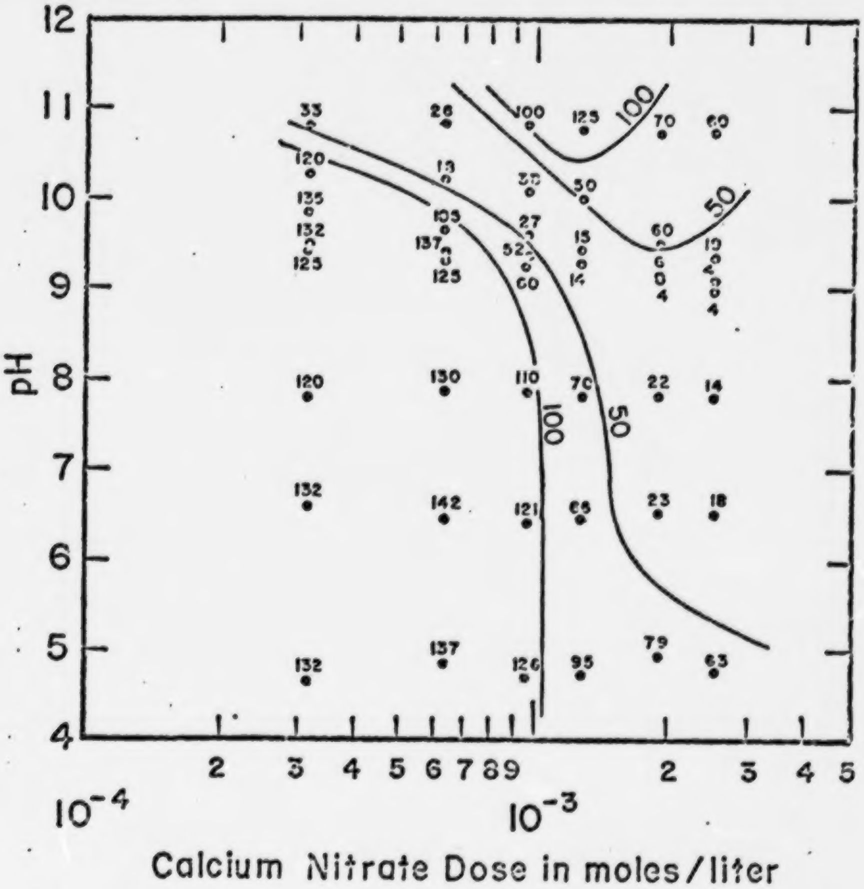

FIGURE V-20. RESIDUAL TURBIDITY CONTOURS FOR 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF pH AND CALCIUM NITRATE DOSE WITH 3.75 mg/l (as $SiO_2$) ACTIVATED SILICA.

Sulfuric acid or sodium hydroxide added with calcium nitrate provided variation in pH values. Turbidities are in Jackson Turbidity Units, JTU.

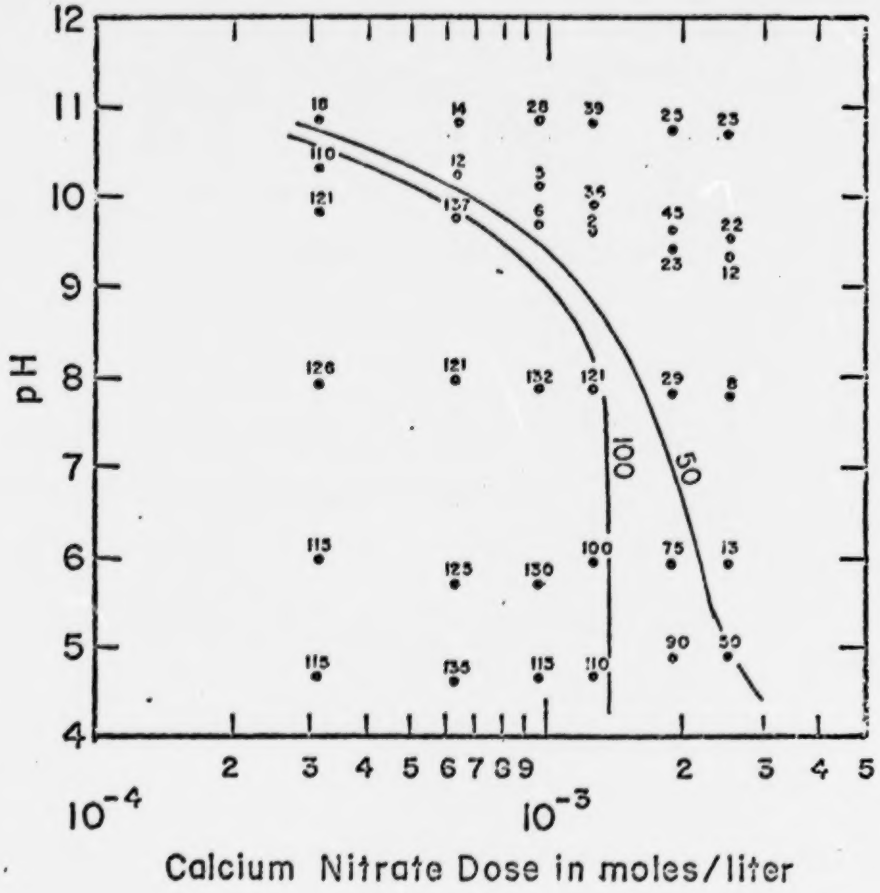

FIGURE V-21. RESIDUAL TURBIDITY CONTOURS FOR 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF pH AND CALCIUM NITRATE DOSE WITH 8.0 mg/l (as $SiO_2$) ACTIVATED SILICA.

Sulfuric acid or sodium hydroxide added with calcium nitrate provided variation in pH values. Turbidities are in Jackson Turbidity Units, JTU.

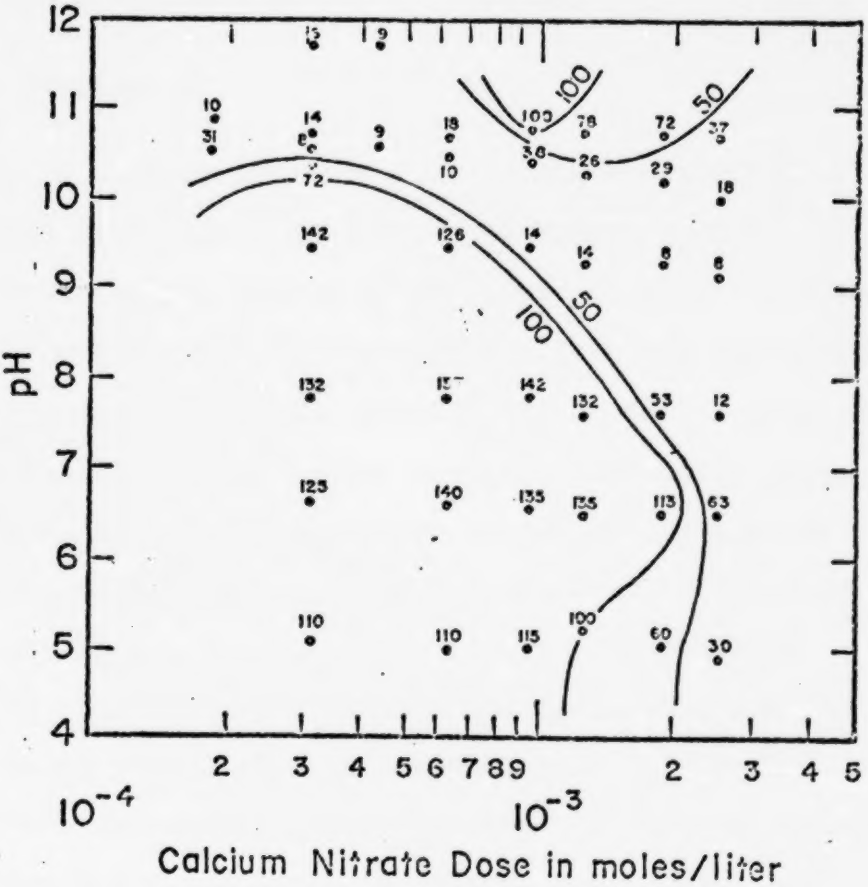

FIGURE V-22. RESIDUAL TURBIDITY CONTOURS FOR 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF pH AND CALCIUM NITRATE DOSE WITH 12.0 mg/l (as $SiO_2$) ACTIVATED SILICA.

Sulfuric acid or sodium hydroxide added with calcium nitrate provided variation in pH values. Turbidities are in Jackson Turbidity Units, JTU.

reversal discussed in a preceding section.

Effect of Phosphates.

Based on some preliminary studies and the results of the mixed synthetic system shown in Figure V-5, a detailed study on the effect of phosphate on clarification using calcium hydroxide and activated silica was conducted. This was accomplished by determining the amount of calcium hydroxide required to halve the original turbidity, $D_{t/2}$, of a 150 mg/l bentonite suspension in $10^{-3}$ molar sodium bicarbonate containing varying concentrations of disodium hydrogen phosphate, $Na_2HPO_4$. The results are shown in Figure V-23 when calcium hydroxide was used alone and with activated silica at a concentration of 3.75 mg/l $SiO_2$. At low concentrations of phosphate activated silica causes significant reduction in calcium hydroxide dosage. As the phosphate concentration is increased, increasing amounts of hydroxylapatite are formed. The hydroxylapatite appears to aid in the clarification. At a phosphate concentration of about 7 x $10^{-4}$ moles per liter (7 mg/l as $PO_4$), the benefit due to hydroxylapatite formed from the phosphate has increased to the point that activated silica additions are no longer necessary. In fact, the addition of activated silica to these systems containing high phosphate levels appears to be slightly detrimental

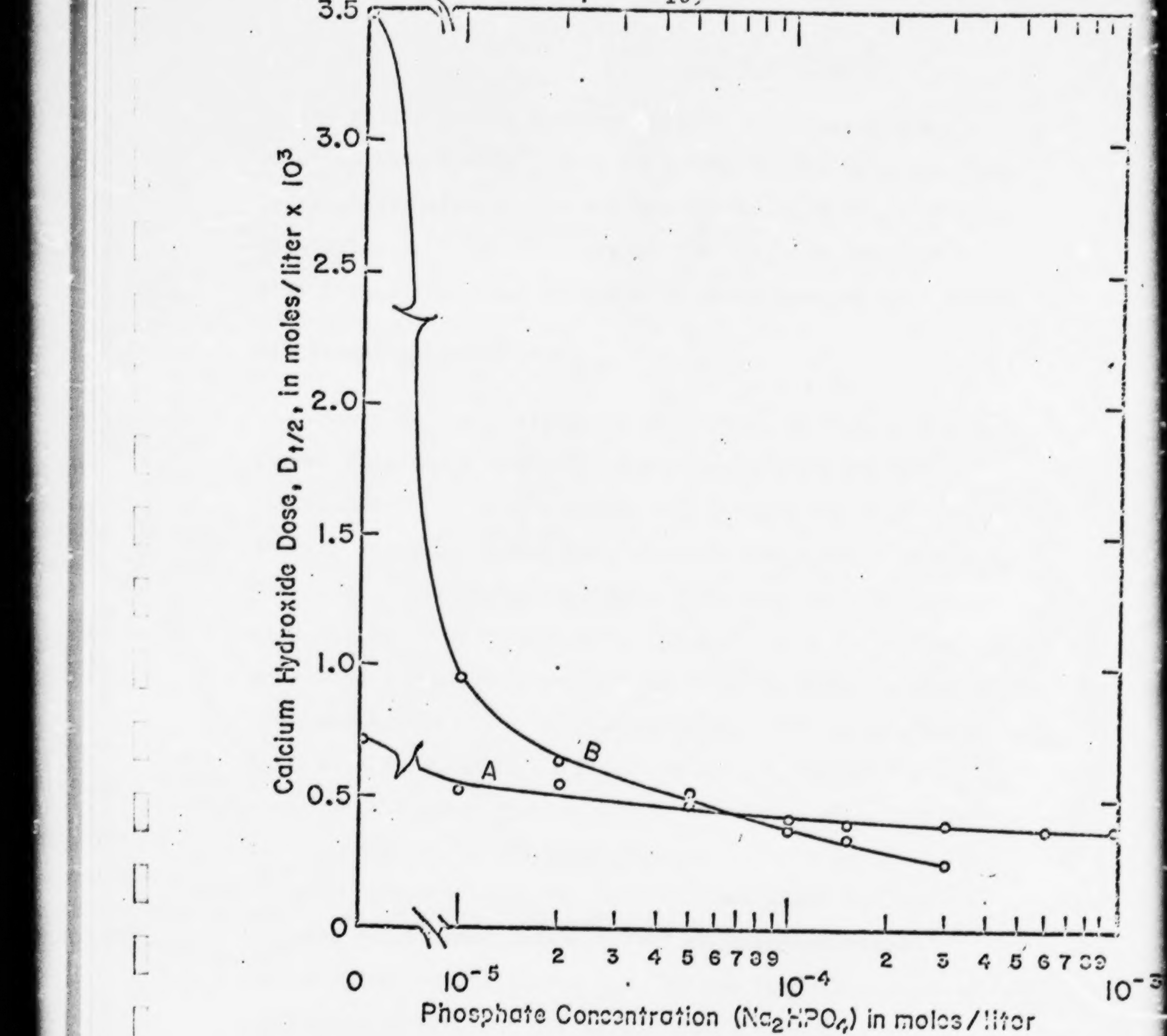

FIGURE V-23. VARIATION OF COAGULANT DOSE REQUIRED TO HALVE THE TURBIDITY ($D_{t/2}$) OF 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS A FUNCTION OF INITIAL PHOSPHATE CONCENTRATION.

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Curve A resulted from treatment with 3.75 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

to the action of the hydroxylapatite in reducing the required lime dosage. This is likely caused by a reaction between activated silica and hydroxylapatite which makes them slightly less effective in reducing the required lime dosage than when only one of these species is present.

Additional Studies.

Based on the preliminary data shown in Figure III-5, it was decided to conduct a study using multinuclear silica made by dilution of one molar stock solution to 0.05 moles per liter $SiO_2$ and used immediately after dilution. This study was conducted using calcium nitrate with varying concentrations of sulfuric acid or sodium hydroxide for pH adjustment. The results shown in Figure V-24 are similar to a comparable study using activated silica aged to 100 JTU shown in Figure V-22, indicating that these multinuclear species are as effective as activated silica prepared by the usual method.

The concentration of bentonite was shown in Figures V-1 and V-2 to have little effect on lime-activated silica treatment, at least for the two concentrations studied, 150 mg/l and 300 mg/l. Additional studies were conducted to verify these findings using calcium nitrate and varying concentrations of sulfuric acid or sodium hydroxide, in place of lime, thus separating

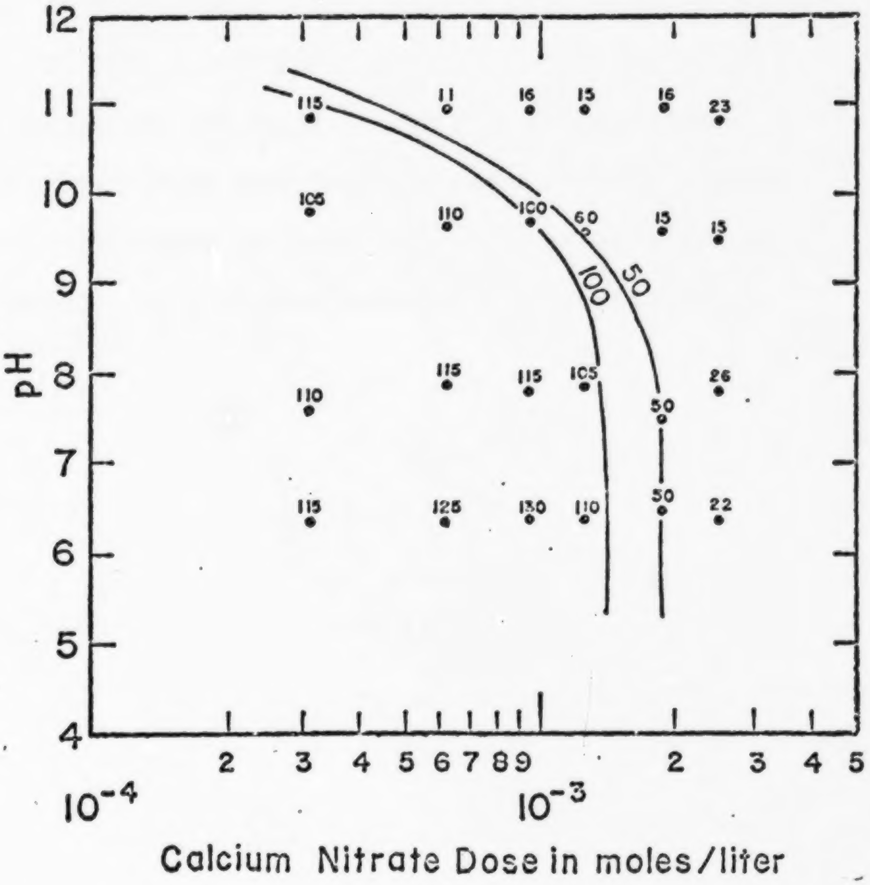

FIGURE V-24. RESIDUAL TURBIDITY CONTOURS FOR 150 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF pH AND CALCIUM NITRATE DOSE WITH 12.0 mg/l (as $SiO_2$) MULTINUCLEAR SILICA.

Sulfuric acid or sodium hydroxide added with calcium nitrate variation in pH values. Turbidities are in Jackson Turbidity Units, JTU.

the effects of calcium addition and pH. The results of a 300 mg/l bentonite suspension are shown in Figure V-25 using no activated silica and Figure V-26 using 3.75 mg/l (as $SiO_2$) activated silica. In comparison, similar studies of 150 mg/l bentonite suspensions shown in Figures V-19 and V-20 indicate little effect, except slightly lower calcium required to clarify the high suspension with higher bentonite concentration.

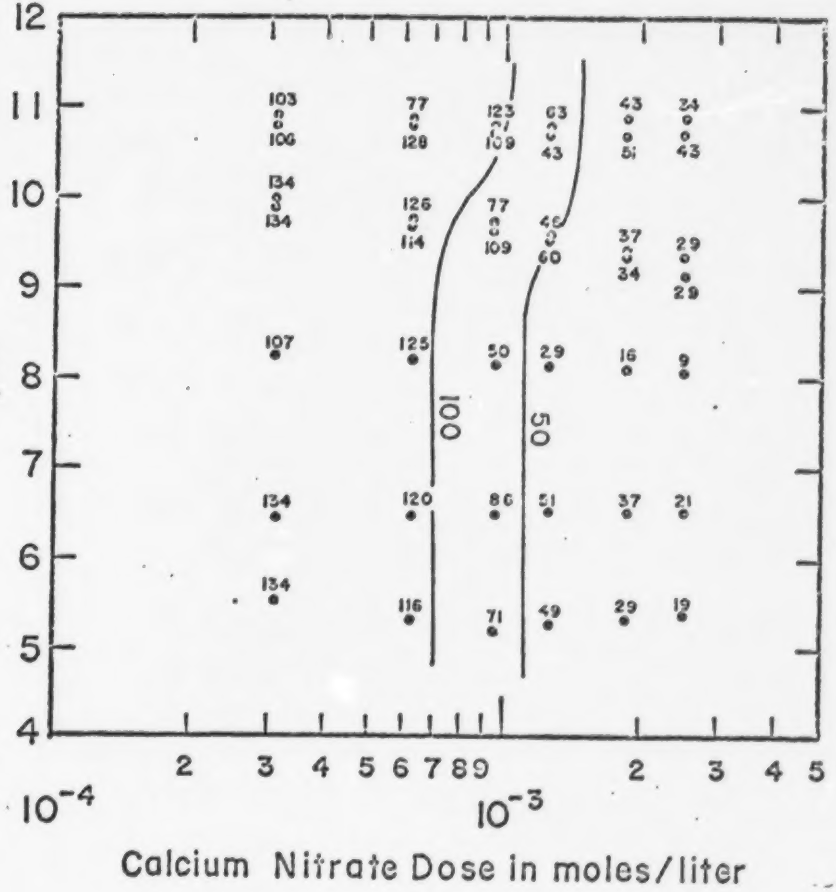

FIGURE V-25. RESIDUAL TURBIDITY CONTOURS FOR 300 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF pH AND CALCIUM NITRATE DOSE.

Sulfuric acid or sodium hydroxide added with calcium nitrate provided variation in pH values. Turbidities are in Jackson Turbidity Units, JTU.

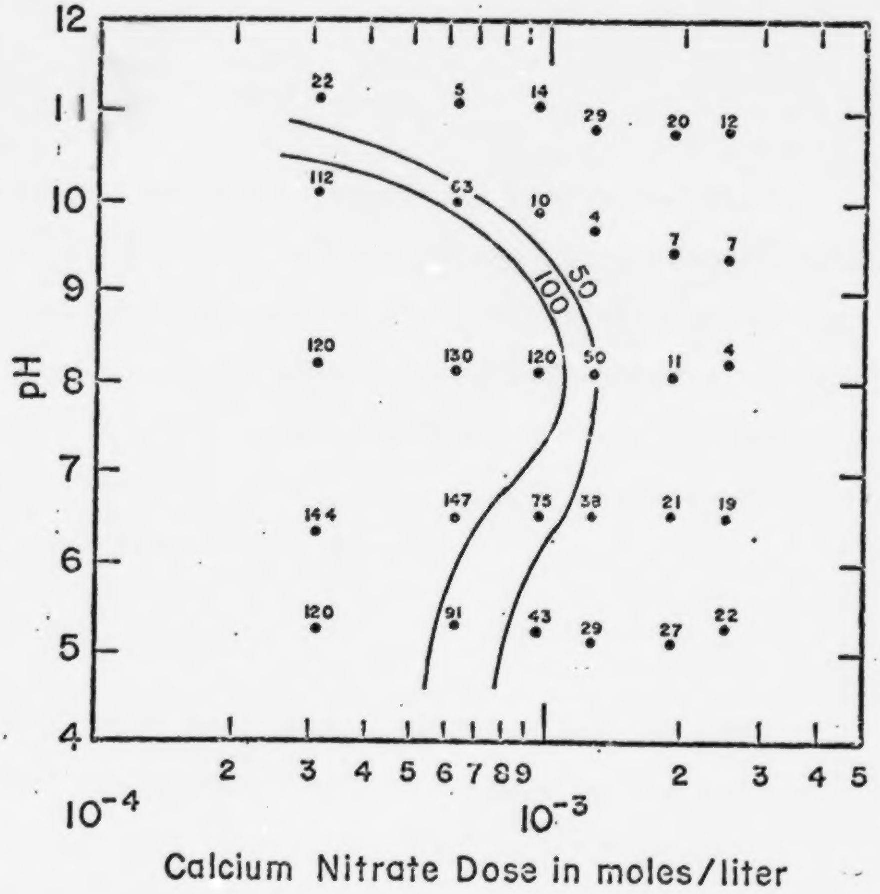

FIGURE V-26. RESIDUAL TURBIDITY CONTOURS FOR 300 mg/l BENTONITE IN $10^{-3}$ MOLAR SODIUM BICARBONATE AS FUNCTIONS OF pH AND CALCIUM NITRATE DOSE WITH 3.75 mg/l (as $SiO_2$) ACTIVATED SILICA.

Sulfuric acid or sodium hydroxide added with calcium nitrate provided variation in pH values. Turbidities are in Jackson Turbidity Units, JTU.

## VI. COAGULATION OF NATURAL WASTEWATERS

### Introduction

Coagulation studies with natural waters and wastewaters were conducted at various stages of the experimental program to confirm findings of the studies with synthetic systems. The four types of natural waters and wastewaters studied were: 1) raw sewage, 2) river water, 3) creek water, and 4) storm water draining from a residential area with paved streets and gutters.

### Results and Discussions

The results of coagulation studies in which lime and activated silica were used to clarify raw sewage from the Ann Arbor Sewage Treatment Plant are shown in Figure VI-1. No reduction in the required lime dosage was observed when silica was added, but floc particles appeared to be larger and settled more rapidly when silica was present. The alkalinity of the wastewater sample represented by the data in Figure VI-1 was not specifically determined, but it can be concluded that the reason for the lack of effectiveness of the scheme in this case was due to high alkalinity. Several raw

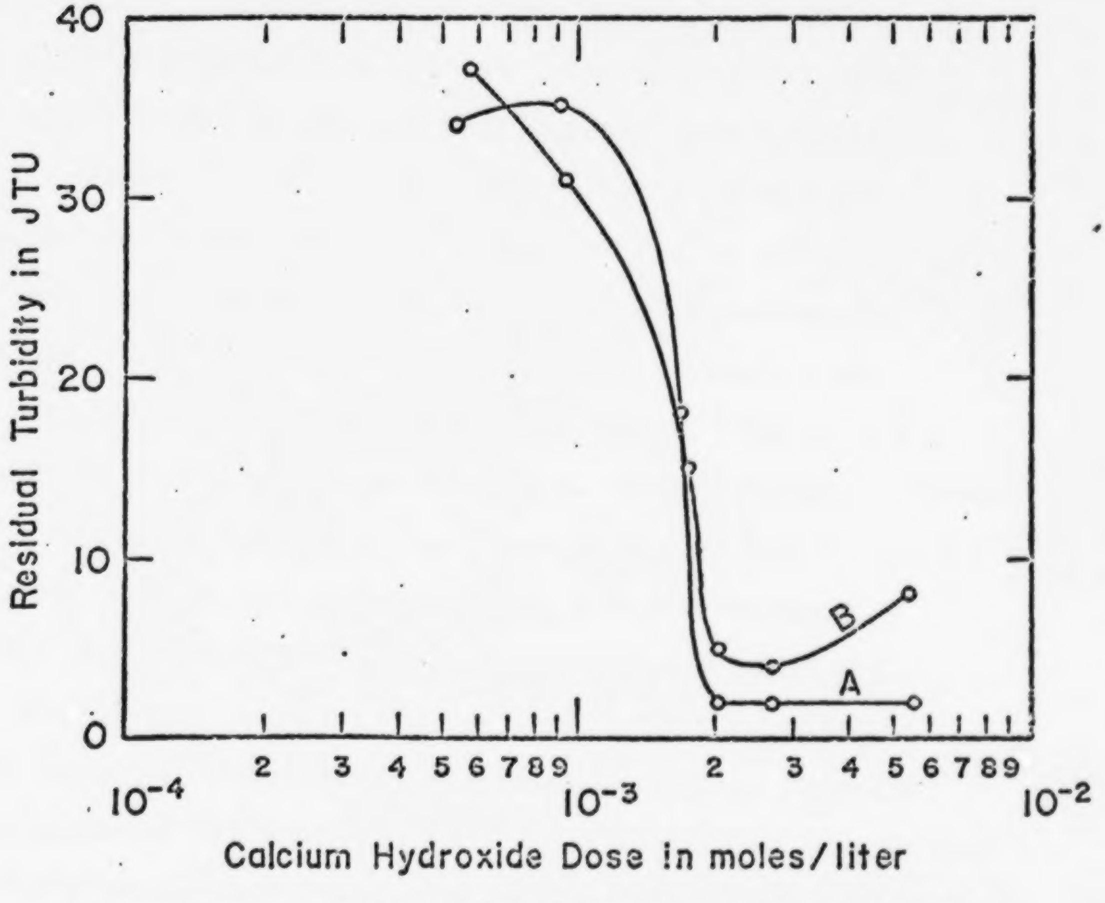

FIGURE VI-1. RESIDUAL TURBIDITY OF RAW SEWAGE AS A FUNCTION OF CALCIUM HYDROXIDE DOSE.

Curve A resulted from treatment with 8.0 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

sewage samples collected subsequently were analyzed and found to have alkalinities of about 200 mg/l as $CaCO_3$. The pH of the original sample was recorded as 7.2, therefore the alkalinity was primarily bicarbonate alkalinity.

A second sample of raw sewage from the same plant was studied using a range of activated silica concentrations. The results are shown in Figure VI-2. No reduction in lime was observed at any of the activated silica concentrations studied (3.75 to 19 mg/l $SiO_2$). The pH and alkalinity conditions were similar to those indicated above.

The second type of natural water studied was collected from the Huron River just above the Sewage Treatment Plant. The turbidity was relatively low, at about 4 JTU, the pH 8.2, and the alkalinity 228 mg/l as $CaCO_3$, which would be primarily as bicarbonate at this pH value. No significant reduction in lime requirement for coagulation was observed in the presence of activated silica, as shown in Figure VI-3. Again, this is probably attributable to the high alkalinity of the water.

To study a lower alkalinity wastewater, water was collected following a storm from a creek which carries storm runoff from both rural and urban areas. The turbidity was 90 JTU, the pH 7.9, and the alkalinity would again be primarily as bicarbonate, at approximately $10^{-3}$ molar concentration, the concentration of the sodium bicarbonate

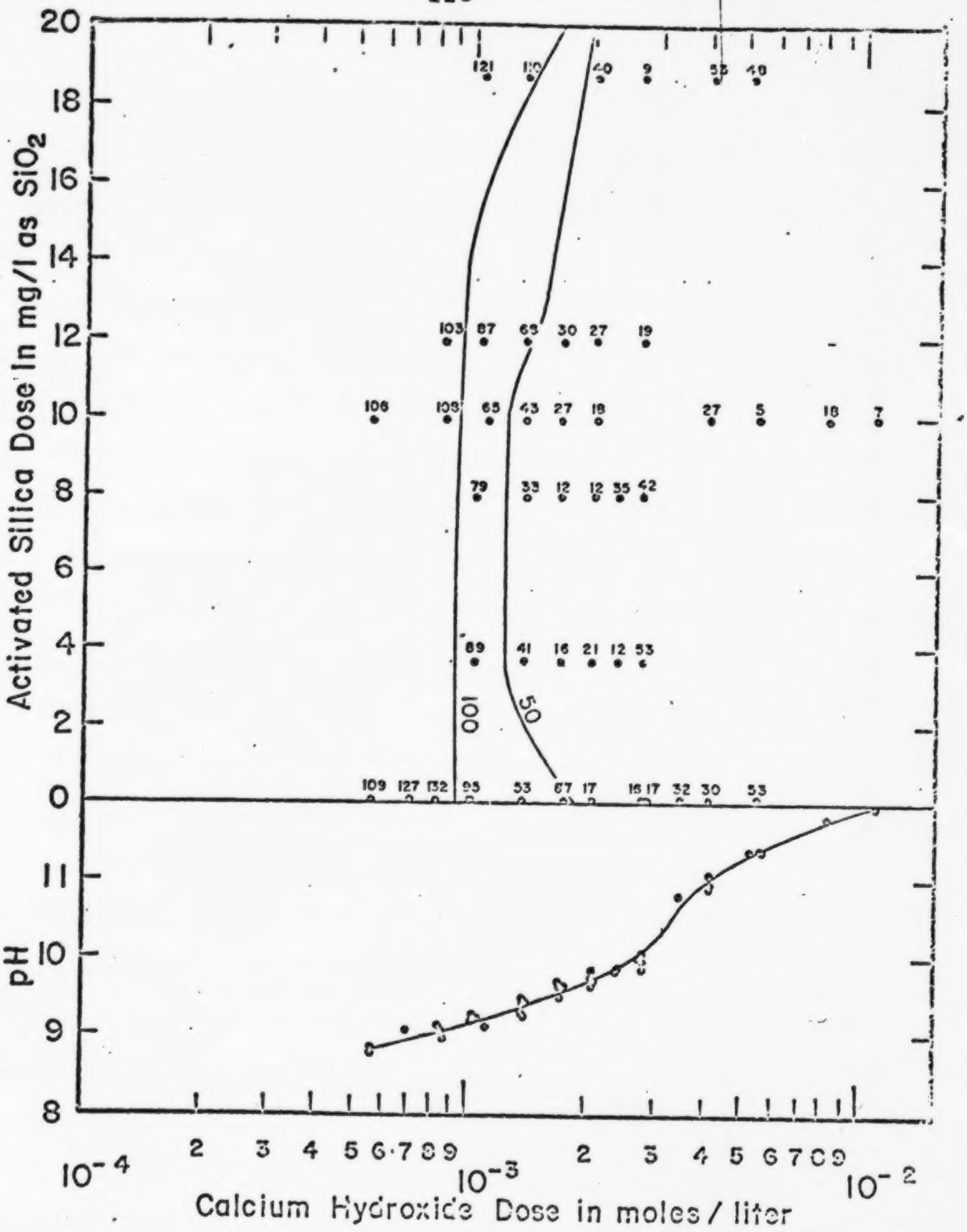

FIGURE VI-2. RESIDUAL TURBIDITY CONTOURS FOR RAW SEWAGE AS FUNCTIONS OF ACTIVATED SILICA AND CALCIUM HYDROXIDE DOSES.

Resulting pH values are also shown as functions of calcium hydroxide dose. Turbidities are in Jackson Turbidity Units, JTU.

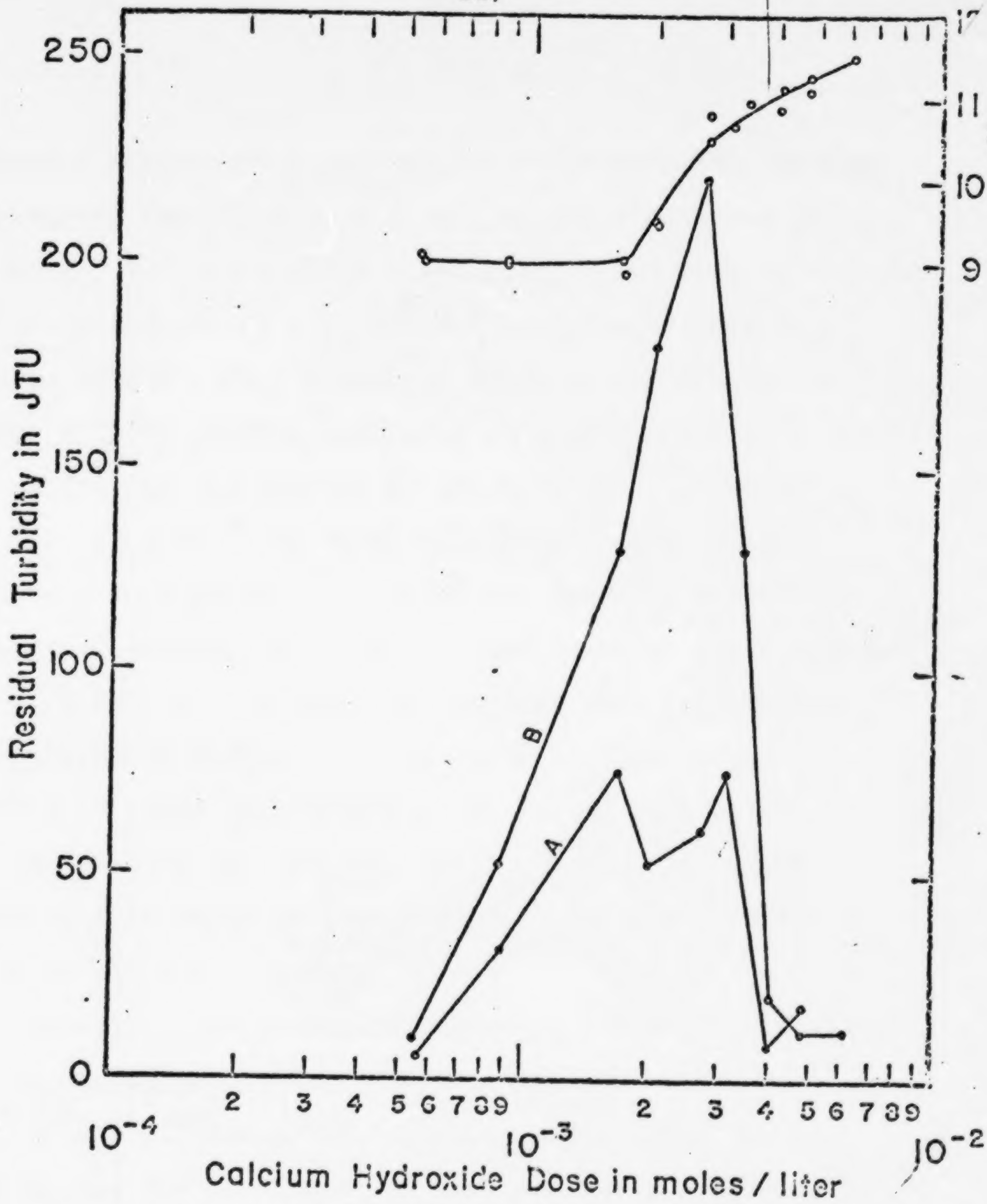

FIGURE VI-3. RESIDUAL TURBIDITY OF RIVER WATER AS A FUNCTION OF CALCIUM HYDROXIDE DOSE.

Resulting pH values are also included and represented by open circles and the right ordinate. Curve A resulted from treatment with 8.0 mg/1 (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium alone.

synthetic experimental systems described earlier. Sodium bicarbonate was added to a second of three aliquots of the sample to increase the alkalinity to 100 mg/l as calcium carbonate ($2 \times 10^{-3}$ molar bicarbonate) and to a third in sufficient amount to increase the alkalinity to 200 mg/l as calcium carbonate ($4 \times 10^{-3}$ molar bicarbonate). The results of the studies on the natural creek water and the two samples in which alkalinity was increased are shown in Figures VI-4 and VI-5. There is a striking similarity between these results and those of the synthetic 150 mg/l bentonite suspensions studied with varying concentrations of sodium bicarbonate, with significant benefit observed when activated silica is used with lime to clarify the low alkalinity waters. As before, no benefit in terms of lime reduction was observed for the high alkalinity waters.

Finally, a water collected from a storm sewer serving a residential area with paved streets, sidewalks, and gutters was studied. The turbidity was 84 JTU, the pH 7.6, and the alkalinity 37 mg/l as $CaCO_3$. The original phosphate level was low, approximately 0.3 mg/l as $PO_4$, and therefore expected to have little effect, as was observed in the studies of the synthetic wastewaters reported in Figure V-23. Significant lime reduction, approximately 10-fold, was found when using activated silica as an aid for clarification of this stormwater.

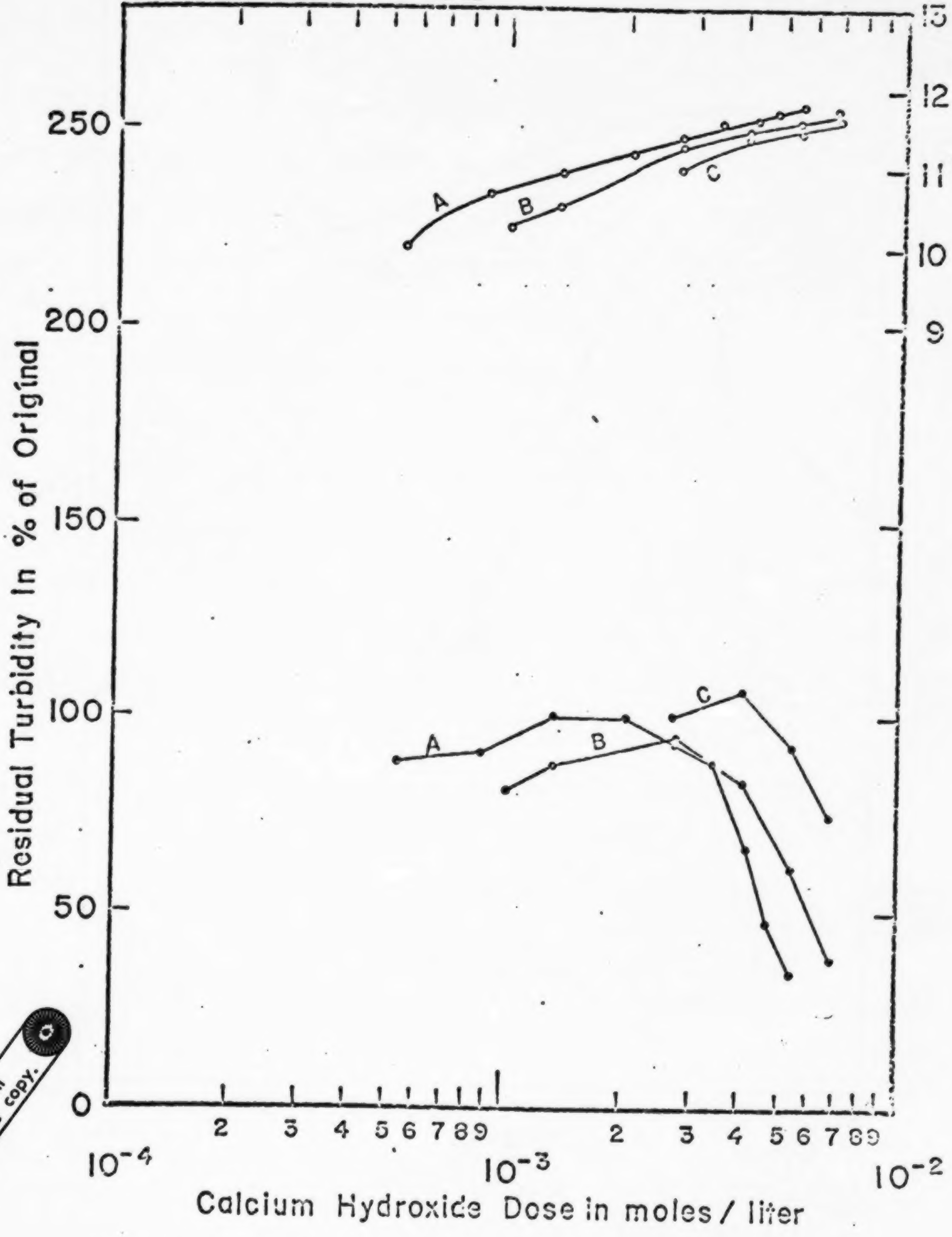

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FIGURE VI-4. RESIDUAL TURBIDITY OF CREEK WATER AS A FUNCTION OF CALCIUM HYDROXIDE DOSE.

Resulting pH values are also included and represented by open circles and the right ordinate. Curve A resulted from treatment of the creek water with a natural alkalinity of 50 mg/l, Curve B from the creek water after sodium bicarbonate had been added to increase the alkalinity to 100 mg/l, and Curve C from the creek water after sodium bicarbonate had been added to increase the alkalinity to 200 mg/l.

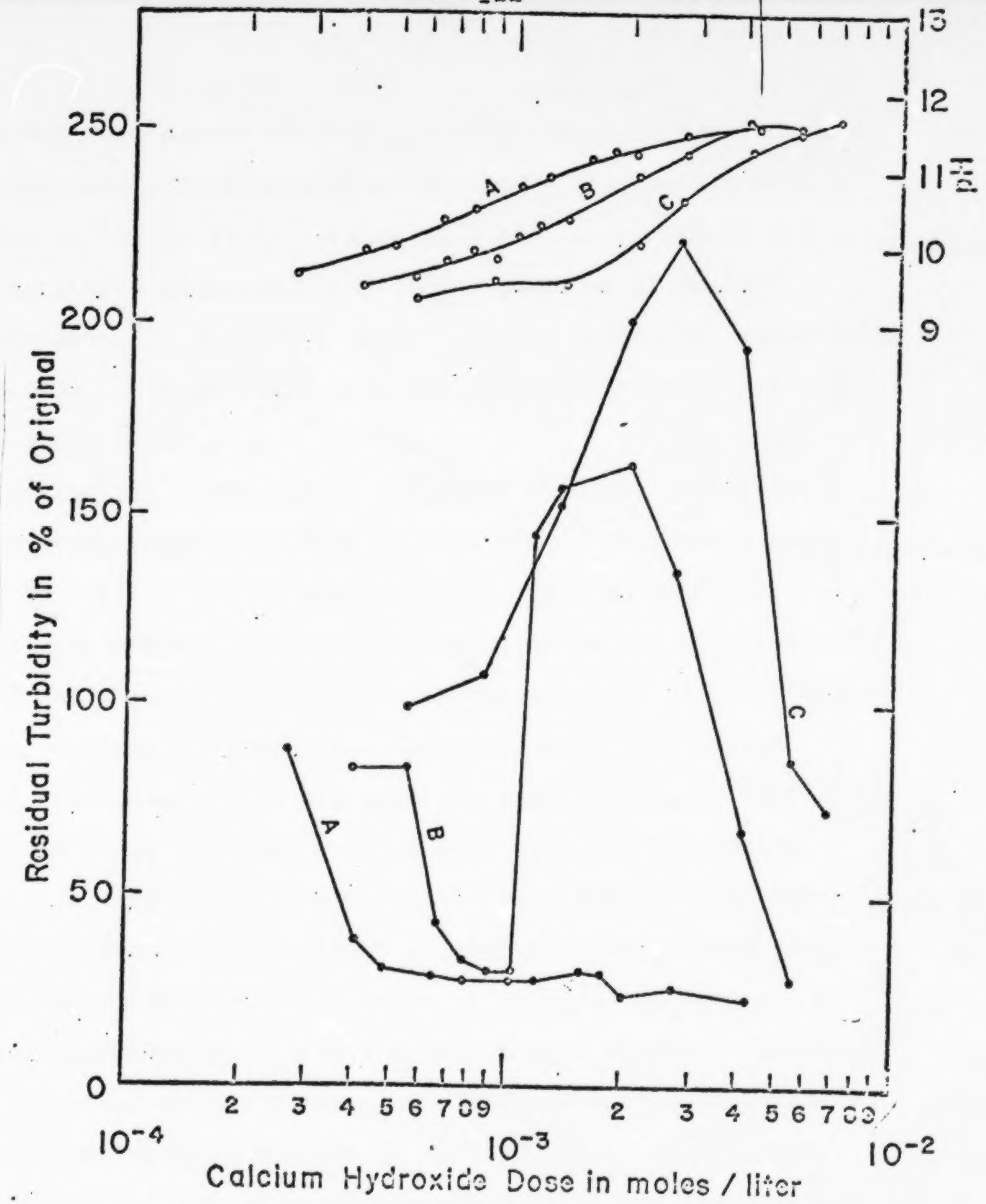

FIGURE VI-5. RESIDUAL TURBIDITY OF CREEK WATER AS A FUNCTION OF CALCIUM HYDROXIDE DOSE WITH 8.0 mg/l (as $SiO_2$) ACTIVATED SILICA.

Resulting pH values are also included and represented by open circles and the right ordinate. Curve A resulted from treatment of the creek water with a natural alkalinity of 50 mg/l, Curve B from the creek water after sodium bicarbonate had been added to increase the alkalinity to 100 mg/l, and Curve C from the creek water after sodium bicarbonate had been added to increase the alkalinity to 200 mg/l.

COD analyses showed no significant increase in the reduction in COD when activated silica was used. The results are shown in Figure VI-6. Figure VI-6 also shows the effect of increased alkalinity due to the addition of sodium bicarbonate to the storm water. These results are essentially the same as those found with the synthetic wastewaters and the creek water.

Finally, a raw sewage collected from the Newton Falls, Ohio Sewage Treatment Plant was studied. This wastewater was relatively low in alkalinity, 95 mg/l as $CaCO_3$, and total phosphates, 7.4 mg/l as $PO_4$. The pH was 7.1, indicating that the alkalinity was primarily bicarbonate alkalinity. Lime required to coagulate this wastewater was reduced when activated silica was used, as shown in Figure VI-7.

In order to study a raw sewage with low alkalinity, an aliquot of the sewage collected from Newton Falls was diluted with an equal volume of distilled water resulting in a wastewater with alkalinity of 48 mg/l as $CaCO_3$ and a total phosphate concentration of 3.8 mg/l as $PO_4$. Again, as was found in the other synthetic and natural wastewaters with alkalinities of about 50 mg/l as $CaCO_3$, significant reduction in lime required for coagulation was found when using activated silica. The results of this study are shown in Figure VI-8.

A settling column study was conducted to compare the settling characteristics of the Newton Falls sewage, after

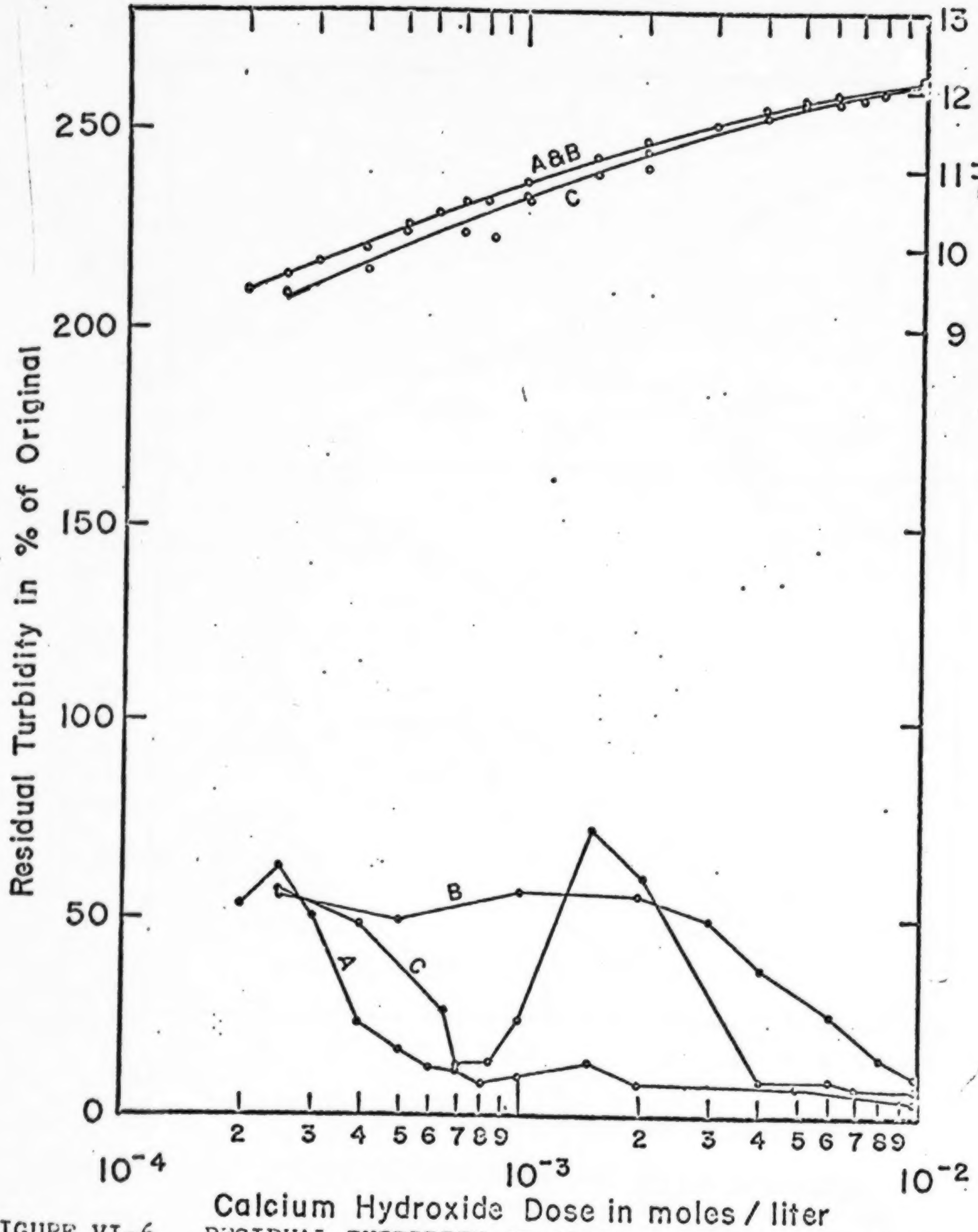

FIGURE VI-6. RESIDUAL TURBIDITY OF STORM WATER AS A FUNCTION OF CALCIUM HYDROXIDE DOSE. Resulting pH values are also included and represented by open circles and the right ordinate. Curve A resulted from treatment with 8.0 mg/l (as $SiO_2$) activated silica and calcium hydroxide, Curve B from calcium hydroxide alone, and Curve C from treatment with 8.0 mg/l (as $SiO_2$) activated silica and calcium hydroxide after the original alkalinity of 37 mg/l was increased to 75 mg/l with sodium bicarbonate.

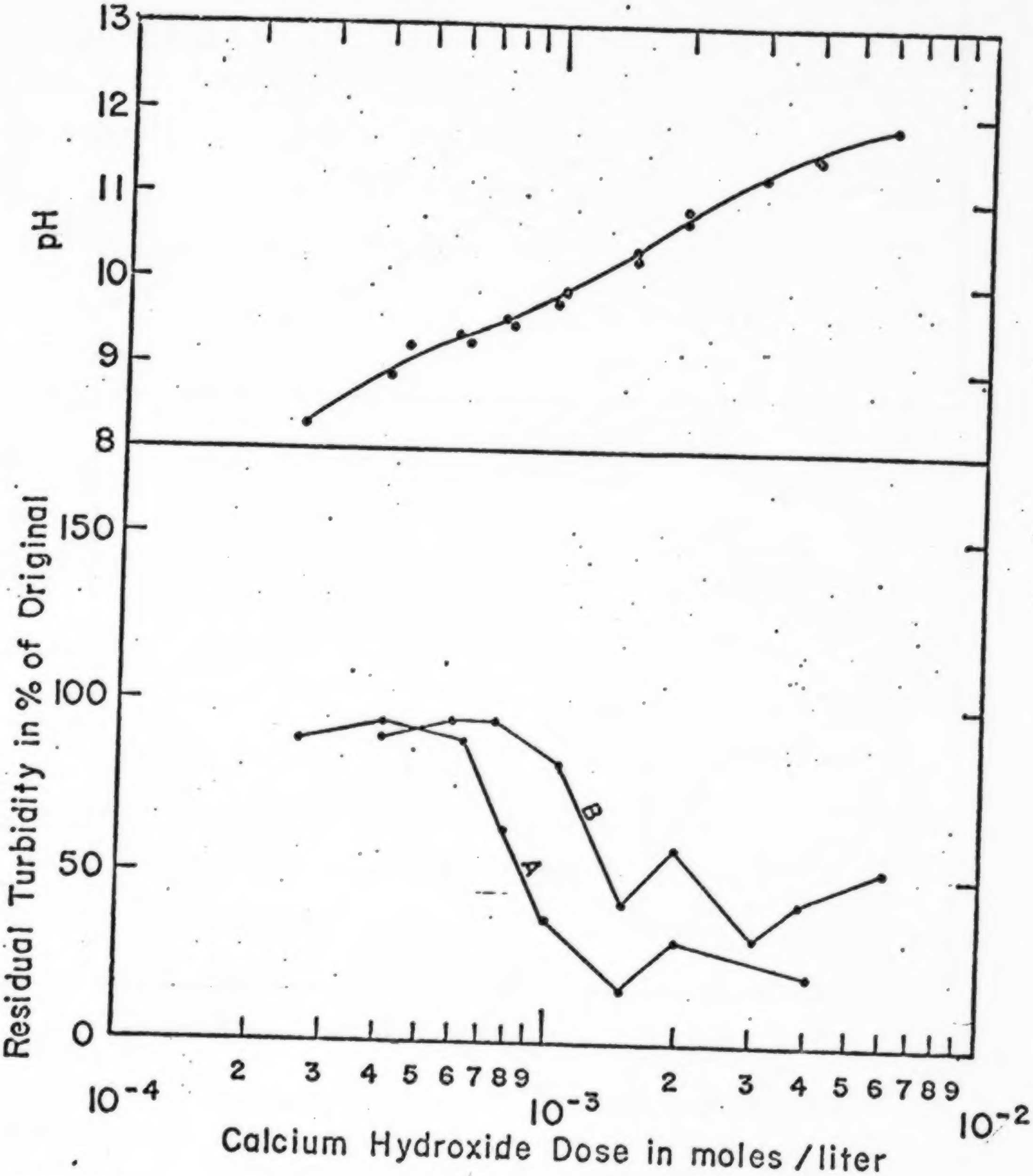

FIGURE VI-7. RESIDUAL TURBIDITY AND pH OF MODERATE ALKALINITY (95 mg/l as $CaCO_3$) SEWAGE AS A FUNCTION OF CALCIUM HYDROXIDE DOSE.

Curve A resulted from treatment with 3.75 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

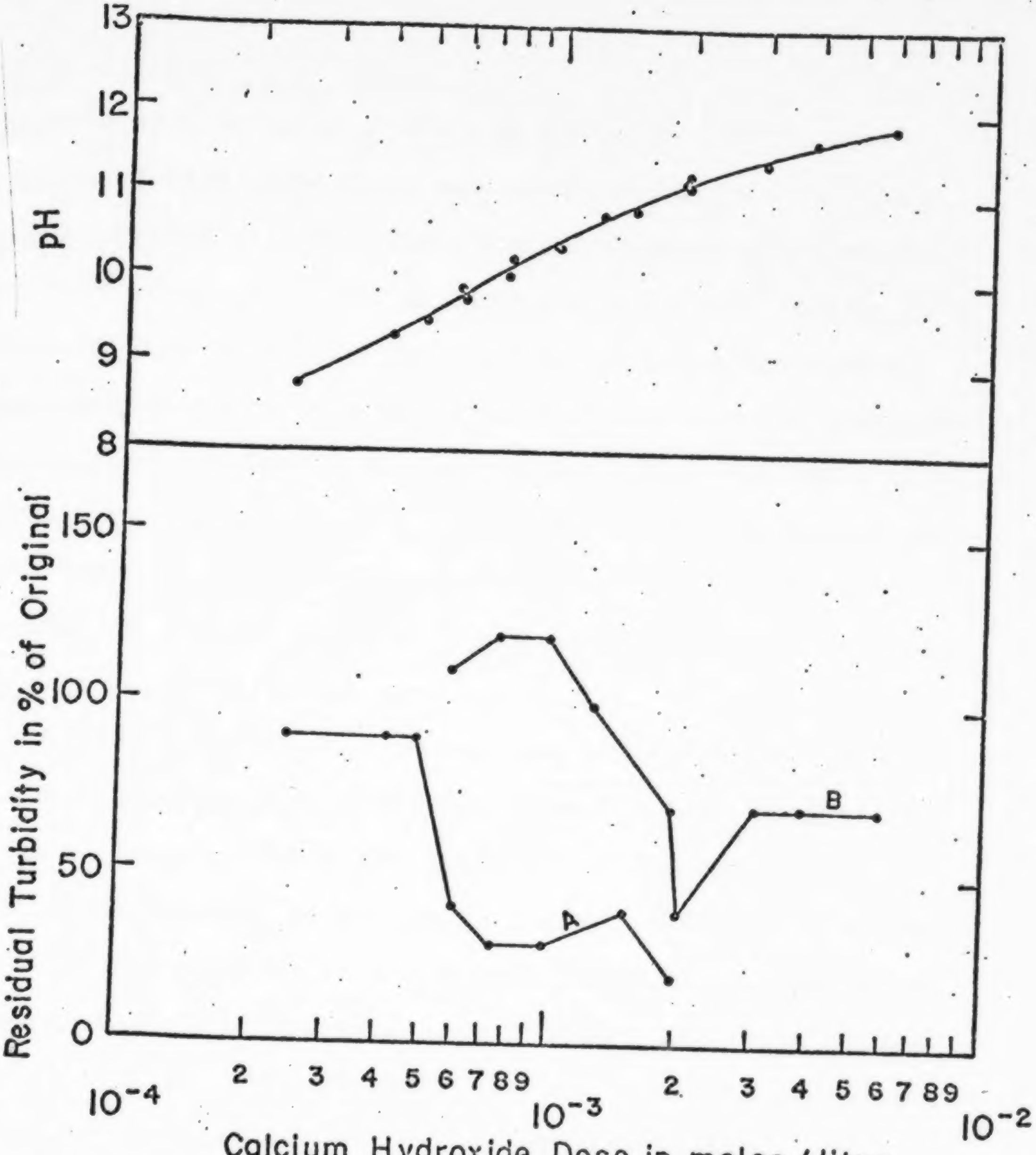

FIGURE VI-8 RESIDUAL TURBIDITY AND pH OF LOW ALKALINITY (48 mg/l as $CaCO_3$) SEWAGE AS A FUNCTION OF CALCIUM HYDROXIDE DOSE.

Curve A resulted from treatment with 3.75 mg/l (as $SiO_2$) activated silica and calcium hydroxide and Curve B from calcium hydroxide alone.

dilution with an equal volume of distilled water, when coagulated with lime alone and when coagulated with lime plus activated silica. The chemical dosages selected were 2 x $10^{-3}$ moles per liter of lime and 7.5 x $10^{-4}$ moles per liter of lime plus 3.75 mg/l (as $SiO_2$) activated silica. These dosages were selected, based on the results shown in Figure VI-8, to assure adequate coagulation for the two methods of treatment. The column was 12.6 centimeters in diameter with four sampling ports located at different depths. Following chemical addition, the wastewater was given a quick mix and a slow mix similar to those used in the jar test procedure. During the settling phase which followed, samples were withdrawn from the four sampling ports at various times and turbidities determined. The results of this study are shown in Figure VI-9. No significant difference in settling and clarification was found. Except, higher turbidities were found in the early stages of settling in the wastewater treated with lime alone, which would be expected due to the higher lime dosage. The time required to reduce the turbidity to a low level (e.g., 5 JTU) at different depths was essentially the same in both cases.

Imhoff cones were used to study sludge volumes resulting from treatment of the Newton Falls sewage after dilution with an equal volume of distilled water. This was accomplished by following the conventional jar test procedure using 2 x $10^{-3}$

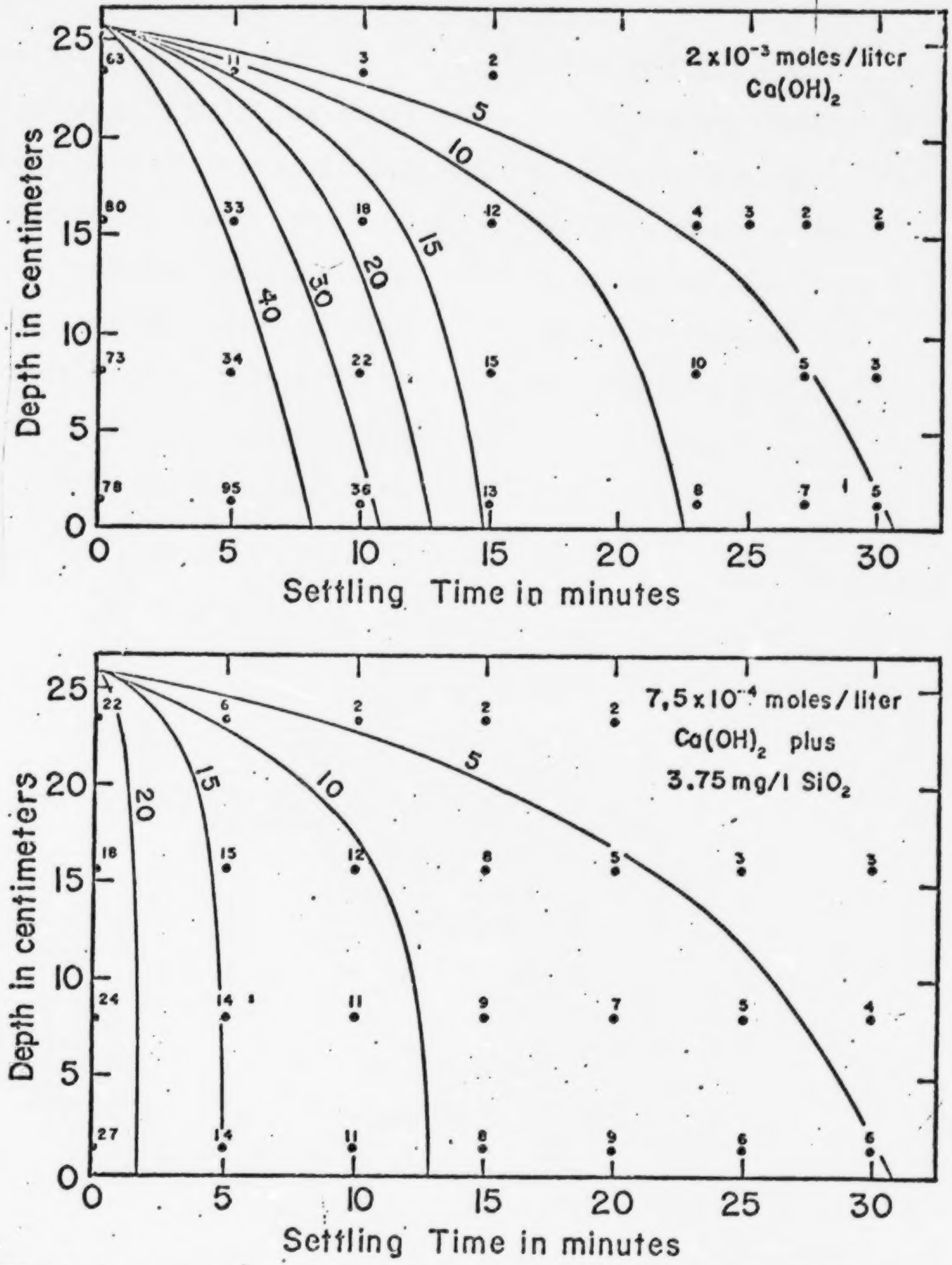

FIGURE VI-9. RESIDUAL TURBIDITY OF LOW ALKALINITY SEWAGE AS A FUNCTION OF SETTLING COLUMN DEPTH AND SETTLING TIME.

Chemical dosage was with lime alone or lime and activated silica as shown. Turbidities are in Jackson Turbidity Units, JTU.

moles per liter of lime, $7.5 \times 10^{-4}$ moles per liter of lime plus 3.75 mg/l (as $SiO_2$) of activated silica, and a control with no chemical addition. After slow mixing the suspensions were transfered by carefully pouring the suspensions from the one-liter beakers into the Imhoff cones with a minimum amount of mixing. Sludge volumes were then recorded as functions of settling time. Substantially greater sludge volumes resulted using coagulation with lime alone as shown in Figure VI-10.

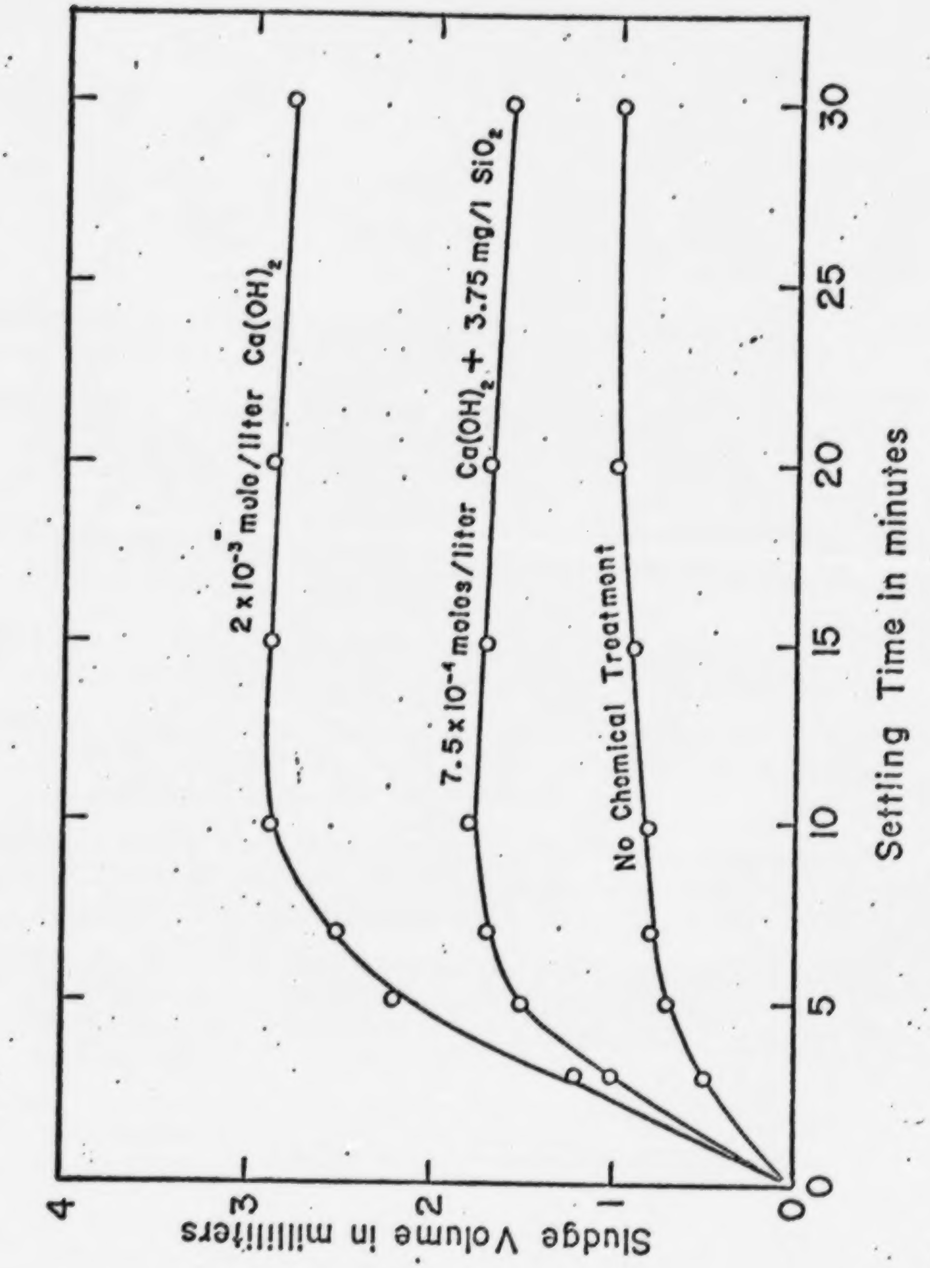

FIGURE VI-10. SLUDGE VOLUMES.

Sludge volumes, measured in Imhoff cones, of 800 ml of sewage with no chemical treatment, after coagulation with $2 \times 10^{-3}$ moles/liter of lime, and after coagulation with $7.5 \times 10^{-4}$ moles/liter of lime plus 3.75 mg/l (as $SiO_2$) activated silica.

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# APPENDIX

## Jar Test Procedure

A Phipps and Bird six-jar variable speed stirrer, illuminated from the bottom by fluorescent bulbs, was used to provide mixing for the coagulation studies.

The mixing and settling procedures, unless otherwise noted, have been conducted as follows:

1. Place 800 milliters of sample in one liter glass beakers.
2. Measure chemical for each sample and store in 5-ml glass cup. Select reagent concentrations to allow the use of one cup or occasionally two. The solubility of calcium hydroxide is too low to use in solution form. To avoid difficulties of maintaining slurries of calcium hydroxide, weigh using an analytical balance, and add appropriate amounts dry to each test sample.
3. Start stirrer mixing samples at 100 rpm and add first chemical additions to each jar in rapid succession by pouring the contents of 5-ml glass cups, then dropping the cup

into the test sample. This is to assure addition of the total contents and rapid dissemination throughout the sample. The first chemical addition, unless otherwise noted, is calcium nitrate or calcium hydroxide. When calcium nitrate is used, pH adjusting reagents are added to each test sample and the cup dropped at the same time as the calcium nitrate. When dry calcium hydroxide is used, it is dumped from dry powder paper followed by a small stream of distilled water from a plastic wash bottle to quickly break up any accumulation on the surface or attached to the shaft of the mixing paddle.

4. After a short period of rapid mixing--two minutes unless dry calcium hydroxide is used, then three minutes--activated silica is added using the 5-ml glass cups, and rapid mixing is continued for one minute.
5. Slow mixing, 30 rpm, is continued for twenty minutes then the mixer is stopped and settling allowed to occur.
6. At the end of ten minutes settling, carefully siphon sample from one inch below the

surface and measure its turbidity using a Hach Model 2100 Turbidimeter or similar instrument.

7. Wherever samples are required for other analyses siphon appropriate amounts from one inch below the surface, without delay, after making the turbidity measurements.
8. Following either the turbidity measurement or additional sample collection, measure pH using a 0 - 14 range glass-calamel electrode couple attached to a Corning Model 20 or similar meter by placing the electrodes directly into the upper portion of the treated sample in the one liter glass beakers.

Chemical Analyses

Chemical analyses for Kjeldahl nitrogen, total phosphate, and chemical oxygen demand (COD) have been made using a Technicon Auto Analyzer. The reagents and procedures used are outlined in the following sections.

Kjeldahl Nitrogen.

Reagents.

1. Digestion Mix.

Dissolve 3.0 g selenium dioxide in

80 ml distilled water. Add 20 ml 68% perchloric acid and 900 ml concentrated sulfuric acid.

2. Sodium Hydroxide, 35%.

Dissolve 350 g sodium hydroxide and 50 g sodium potassium tartrate in distilled water, then dilute to one liter.

3. Sodium Hypochlorite.

Use the commercial product, "Chlorox".

4. Alkaline Phenol.

Add 276 ml liquified phenol (about 88%) to 500 ml 40% solution of sodium hydroxide, cautiously while cooling, then dilute to one liter with distilled water.

5. Nitrogen Standard.

Dissolve urea in distilled water and dilute to desired concentration based on theoretical concentration of nitrogen.

Procedure.

See flow diagram shown on Figure A-1.

Total Phosphate.

Reagents.

1. Digestion Mix.

Dissolve 0.5 g vanadium pentoxide in 80 ml distilled water. Add 20 ml 68%

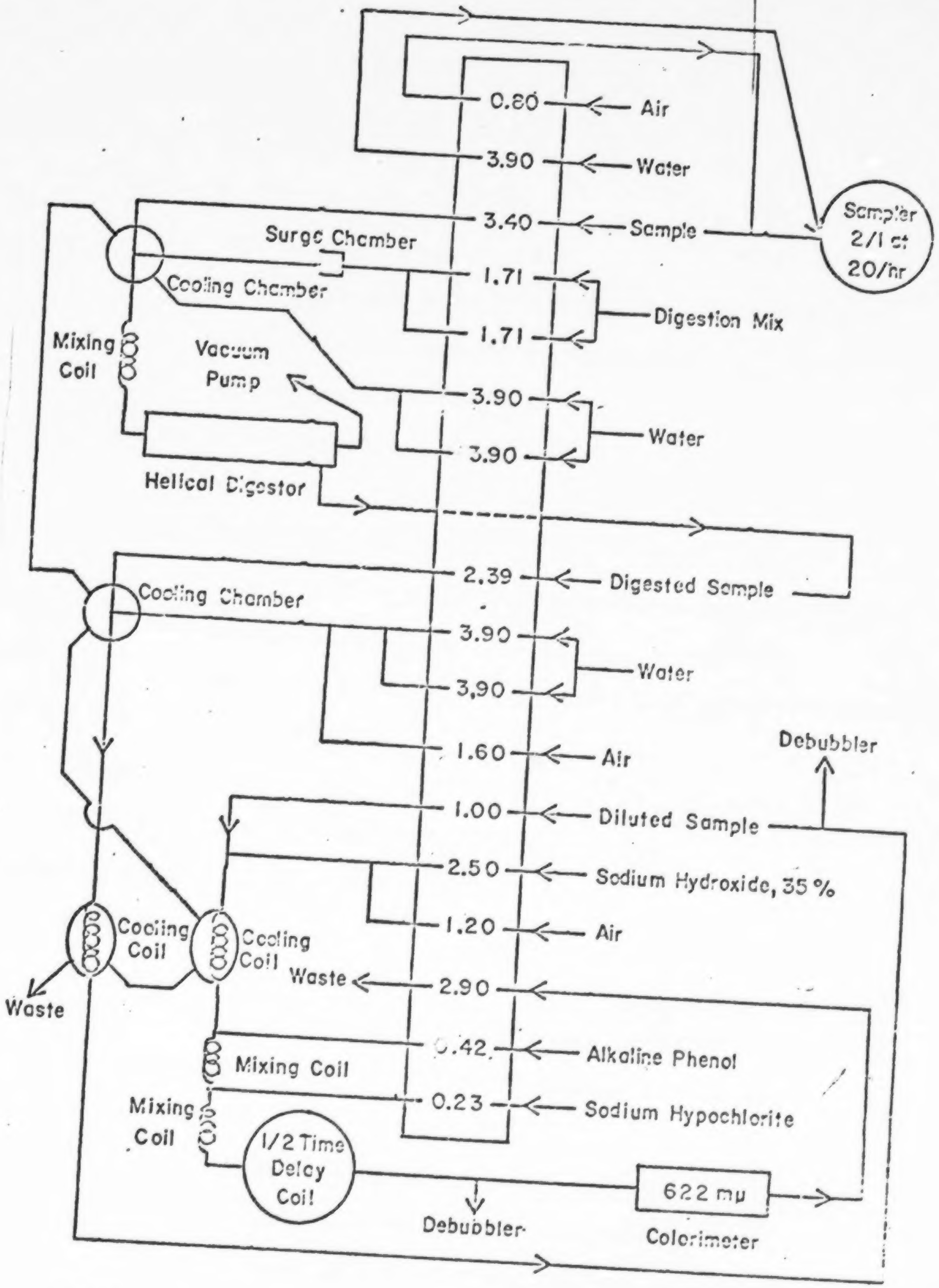
0.80
Air
3.90
Water
3.40
Sample
Sampler 2/1 ct 20/hr
Surge Chamber
1.71
Cooling Chamber
1.71
Digestion Mix
Mixing Coil
Vacuum Pump
3.90
Water
3.90
Helical Digestor
2.39
Digested Sample
Cooling Chamber
3.90
Water
3,90
1.60
Air
Debubbler
1.00
Diluted Sample
2.50
Sodium Hydroxide, 35 %
1.20
Air
Cooling Coil
Cooling Coil
Waste
2.90
Waste
0.42
Alkaline Phenol
Mixing Coil
Mixing Coil
0.23
Sodium Hypochlorite
1/2 Time Delay Coil
622 mμ
Debubbler
Colorimeter

FIGURE A-1. AUTO ANALYZER FLOW DIAGRAM FOR KJELDAHL NITROGEN ANALYSES.

perchloric acid and 900 ml concentrated sulfuric acid.

2. Ammonium Molybdate, 1%.

   Dissolve ammonium molybdate in distilled water then dilute to 1% by weight.

3. Hydrazine Sulfate, 0.2%.

   Dissolve hydrazine sulfate in distilled water then dilute to 0.2% by weight.

4. Phosphate Standard.

   Dissolve anhydrous potassium dihydrogen in distilled water and dilute to desired concentration based on theoretical concentration of phosphate.

Procedure.

See flow diagram shown on Figure A-2.

Chemical Oxygen Demand, COD.

Reagents.

1. Digestion Mix.

   Add ml 0.25 N potassium dichromate and 875 ml concentrated sulfuric acid to 65 ml distilled water.

2. Mercury (II) Sulfate.

   Dissolve anhydrous dextrose in distilled water and dilute to desired concentration based on the theoretical chemical oxygen demand.

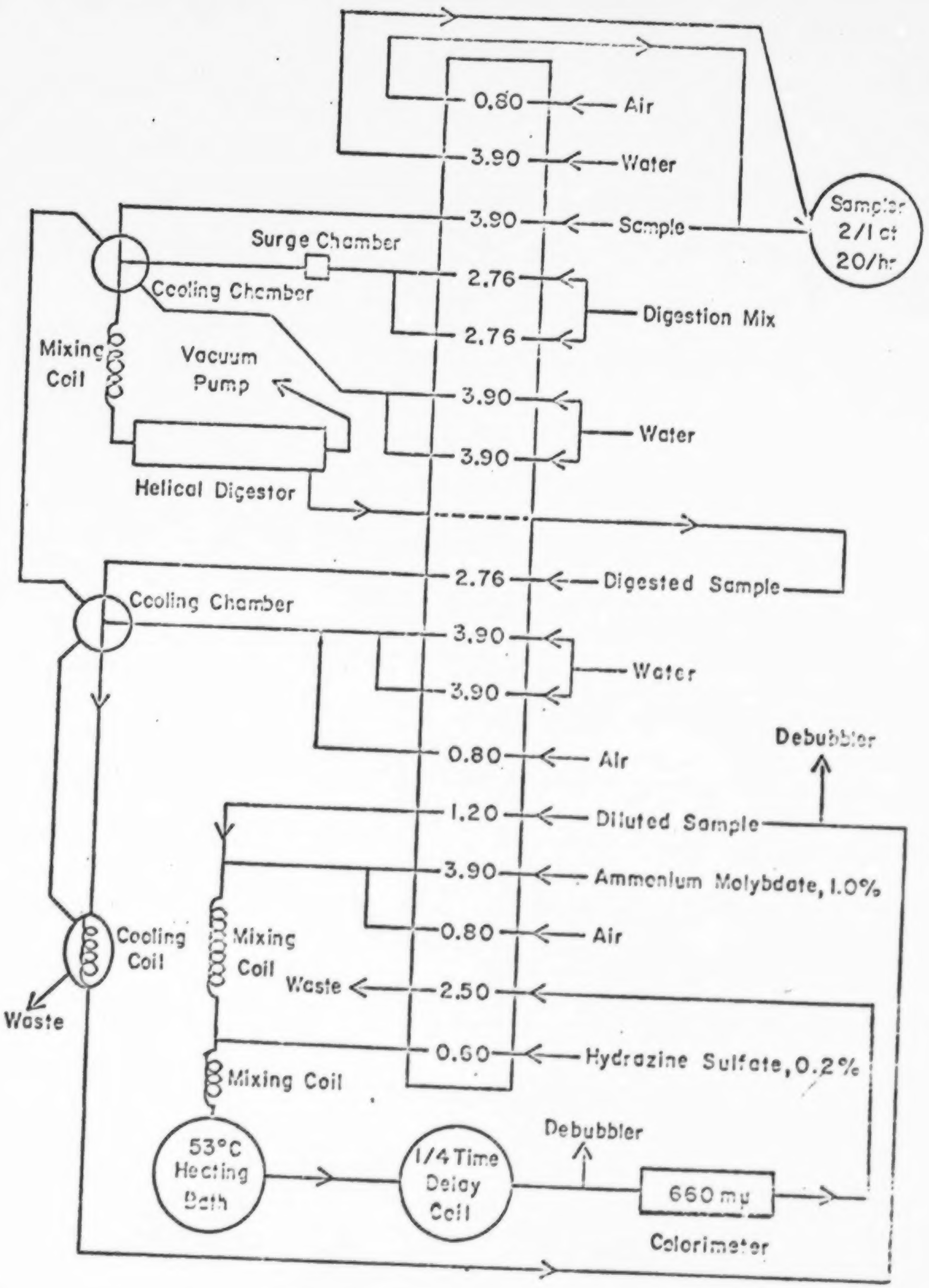
0.80
Air
3.90
Water
3.90
Sample
Sampler 2/1 ct 20/hr
Surge Chamber
2.76
Cooling Chamber
2.76
Digestion Mix
Mixing Coil
Vacuum Pump
3.90
3.90
Water
Helical Digestor
2.76
Digested Sample
Cooling Chamber
3.90
3.90
Water
0.80
Air
Debubbler
1.20
Diluted Sample
3.90
Ammonium Molybdate, 1.0%
0.80
Air
Cooling Coil
Mixing Coil
Waste
2.50
Waste
0.60
Hydrazine Sulfate, 0.2%
Mixing Coil
53°C Heating Bath
1/4 Time Delay Coil
Debubbler
660 mμ
Colorimeter

FIGURE A-2. AUTO ANALYZER FLOW DIAGRAM FOR TOTAL PHOSPHATE ANALYSES.

Procedure.

See flow diagram shown on Figure A-3.

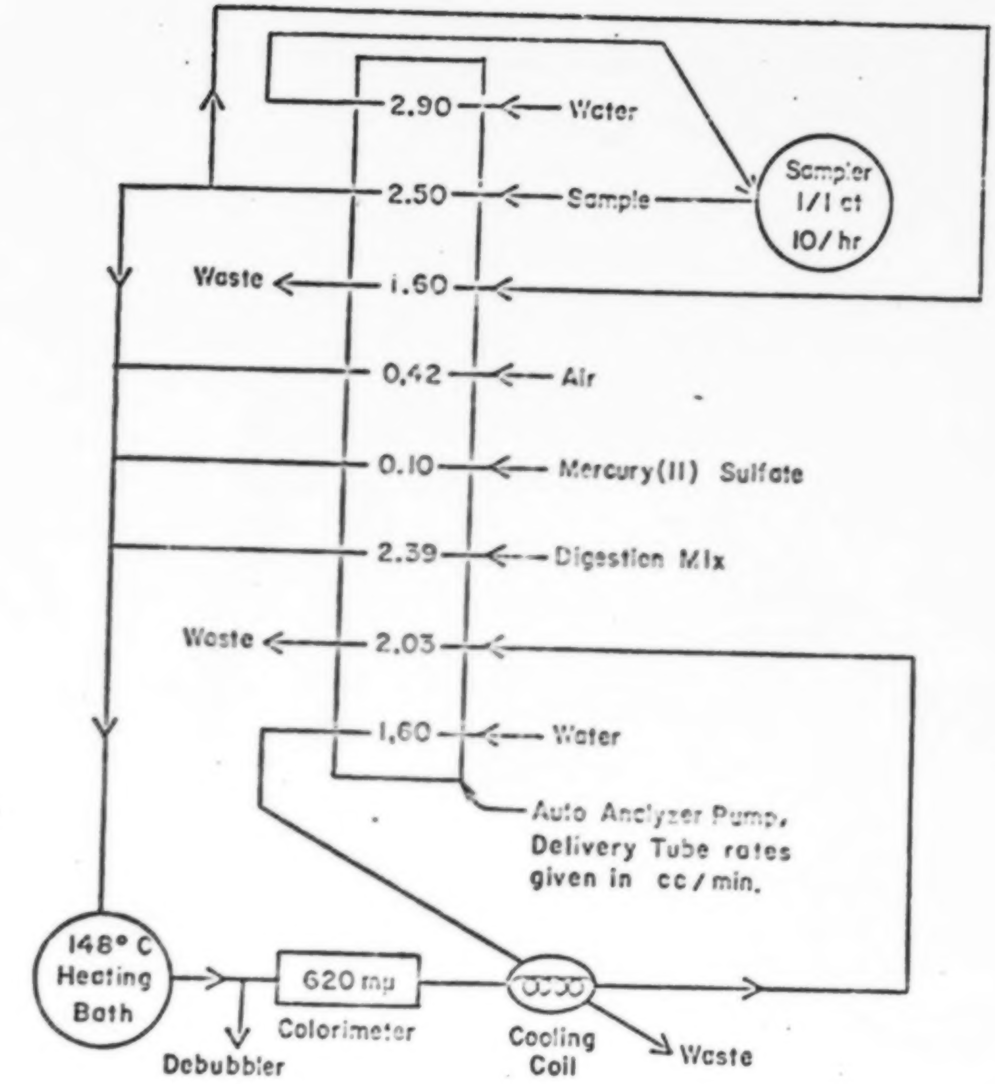
2.90
Water
Sampler
1/1 ct
10/hr
2.50
Sample
Waste
1.60
0.42
Air
0.10
Mercury(II) Sulfate
2.39
Digestion Mix
Waste
2.03
1.60
Water
Auto Analyzer Pump, Delivery Tube rates given in cc/min.
148° C Heating Bath
620 mµ
Colorimeter
Debubbler
Cooling Coil
Waste

FIGURE A-3. AUTO ANALYZER FLOW DIAGRAM FOR CHEMICAL OXYGEN DEMAND ANALYSES.